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URANIUM
TAILINGS
PROGRAM

Canada

GEOCHEMICAL BEHAVIOUR OF VARIOUS NON-RADIONUCLIDE CONTAMINANTS IN URANIUM MILL TAILINGS

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SUMMARY AND RECOMMENDATIONS

Arsenic and nickel occur in some uranium tailings in Saskatchewan up to concentrations of two percent. The arsenides and sulphides in the original ore dissolve and oxidize to a significant degree during the sulphuric acid leach process in the mill. The concentrations of arsenic and nickel that attain levels of g/L in the mill (at Key Lake) are reduced to mg/L and lower levels during lime neutralization prior to discharge of the tailings.

The arsenic concentrations in tailings pore water are likely controlled by adsorption onto aluminum and ferric hydroxide solids. Results of adsorption modelling using independent adsorption and surface protonation constants support this hypothesis. There are major uncertainties concerning the potential lack of identification of arsenate solids that may play a role in controlling concentrations in solution. Aside from protonated species, aqueous complexes are unknown. The oxidation state of arsenic plays an important role in limiting solubility. In general, the oxidized form (As(+5)) is less soluble as metal salts, and is also more readily adsorbed than the more reduced form (As(+3)). When these species are not distinguished in water samples, it is difficult to interpret the potential controls on solubility of As overall.

Nickel solubility appears to be controlled by different mechanisms in different environments. The formation of solid $Ni(OH)_2$ has been recognized to limit nickel concentrations in solution, especially where experimental systems are involved and fresh precipitation has occurred. It has been postulated that nickel ferrite controls nickel solubility in soils where interaction with ferric hydroxide material is important. The predicted behaviour of nickel in solution is similar for both $Ni(OH)_2$ and nickel ferrite. In addition to control by solids, adsorption and coprecipitation mechanisms are probably important in some environments, especially in lake and estuary sediments. Important nickel complexes include $NiSO_4^o$ and $NiCO_3^o$ which may increase total nickel concentrations in solution by a factor of two under certain conditions.

The geochemistry of the elements cobalt, molybdenum and vanadium are complex. Cobalt behaves in a manner similar to nickel and suffers from the same major uncertainties. Molybdenum solution chemistry is relatively well known for the oxidized (+6) form, but information on the (+3) form and possible limiting solids is lacking. Vanadium can exist in solution in three different oxidation states, each with a number of

hydrolysis species. The chemistry of the vanadate form (VO_4^{3-}) is relatively well known, whereas the other oxidation states and solubility controls have not been closely investigated.

The results of this review suggest that certain areas require further consideration to increase our knowledge of the controls on arsenic and nickel solubility in and around the tailings environment. It is recommended that:

- ferric arsenate solids be studied in more detail to characterize the precipitated solids and differentiate between solids formation and adsorption behaviour;
- use be made of indirect evidence of ion activity products in tailings discharge and pore water to study the potential existence of solids that have been identified in nature but not in experimental studies;
- equilibrium adsorption experiments be conducted on appropriate materials over varying pH and total arsenic conditions to verify the adsorption model approach;
- experiments be conducted on freshly discharged tailings involving the extraction and analysis of pore water over time, during which aging of solids can occur or equilibration can be obtained; this would be useful for both arsenic and nickel concentrations which show some variability in behaviour depending on where the water sample is collected in the tailings discharge system;
- the residual arsenide and sulphide minerals containing As and Ni be quantified in the tailings; and
- because arsenite (+3) behaves in a sufficiently different manner than arsenate (+5), that the former be analyzed to determine its importance in tailings discharge and pore water.

1.0 INTRODUCTION

Arsenic and nickel comprise up to two percent by weight of tailings from some uranium ore deposits in Saskatchewan. Both elements exhibit toxic characteristics in the environment and may potentially be released from the tailings to ground and surface water. The controls on the aqueous concentrations of these elements must be known in order to predict releases and potential impacts to the surrounding environment.

This study was conducted to review the geochemical controls on arsenic and nickel concentrations in the discharge from uranium tailings. Thermodynamic data were the primary focus of this review, but other aspects included adsorption behaviour and kinetic behaviour, as well as evidence from laboratory and field studies that suggested controlling factors. In addition to arsenic and nickel, some information on cobalt, molybdenum and vanadium behaviour was also collected.

An intensive survey was conducted with the aid of on-line computer data base searches and assistance from professional library research staff. Use of personal contacts with researchers interested in associated study areas was also made. After compiling thermodynamic data and other relevant information, a consistent thermodynamic data set was established for arsenic and nickel. From this data, thermodynamic calculations were performed and equilibrium concentrations for both substances were found as a function of specific complexes and controlling solids. Available data on arsenic and nickel concentrations in tailings pore water immediately discount certain solids as controlling dissolved concentrations of these substances through equilibrium processes. By this means, many solids that are much too soluble are dismissed, as are those that suggest concentrations that are much lower than those observed. This study, therefore, focuses on the findings that represent reasonable potential for explaining the mechanisms controlling concentrations in a tailings system and surrounding environment.

Other groups contributed to the content of the final report. Melis Consulting Engineers Ltd. provided a review of the characteristics of uranium ore and milling procedures including mineralogical compositions (see Appendix A). Dr. Robert Lemire of AECL (WNRE) constructed and evaluated a consistent thermodynamic data base for arsenic and nickel based largely on information, references and data provided by BEAK (see Appendix B). Senes Consultants Ltd. advised on some issues of arsenic and nickel chemistry and collected some reference material.

This report includes an introduction to uranium ores that contain arsenic and nickel, with emphasis on the mineralogy in the ores. The geochemical controls on arsenic and nickel concentrations in aqueous systems is then presented. Finally, the compiled data are discussed in terms of confidence associated with them, importance of the data in predicting behaviour and major uncertainties involved. This report, therefore, is a guide to what is known with regard to arsenic and nickel behaviour in low-temperature aqueous systems, as well as what further information is required to reliably model the behaviour of these chemical constituents.

2.0 URANIUM ORES AND TAILINGS

2.1 Introduction

The nickel-arsenic type uranium orebodies in Canada are all located within the Athabasca Basin in northern Saskatchewan (Figure 2.1). These deposits are significantly higher grade than the uranium deposits in the Elliot Lake region of northern Ontario and are also accompanied by a significantly different mineralogical make-up.

Of the three northern Saskatchewan producers only Cluff Mining processes a relatively "clean" ore which does not contain arsenic or nickel minerals with the pitchblende uranium mineralization. The Key Lake deposit and the Collins Bay B-Zone deposit contain significant amounts of non-radionuclide contaminants with the uranium mineralization. The Rabbit Lake ore, which is nearly depleted at the Eldor Mines operation, is comparable to the Cluff Lake ore with respect to the low nickel and arsenic content.

There is currently on-going uranium exploration in northern Saskatchewan with several nickel-arsenic bearing high-grade uranium deposits having been indentified to date. By far the most important deposit in terms of total uranium content and grade is the Cigar Lake deposit. Other deposits of significance include the Midwest deposit, Dawn Lake and McLean Lake.

2.2 Mineralogy of Ores

Key Lake

The Key Lake mine, operated by Key Lake Mining Corporation of Saskatoon, Saskatchewan, is located approximately 240 km north of LaRonge, Saskatchewan, 70 km east-southeast of Cree Lake. The Key Lake uranium deposit consists of two separate orebodies, the Gaertner orebody and the Deilmann orebody. Both orebodies contain uranium mineralization associated with nickel arsenides.

The uranium ore minerals include euhedral and radially textured pitchblende (U_3O_8), and smaller amount of coffinite ($U(SiO_4)_{1-x}(OH)_{4x}$). Gersdorffite (Ni,Co) AsS) is the

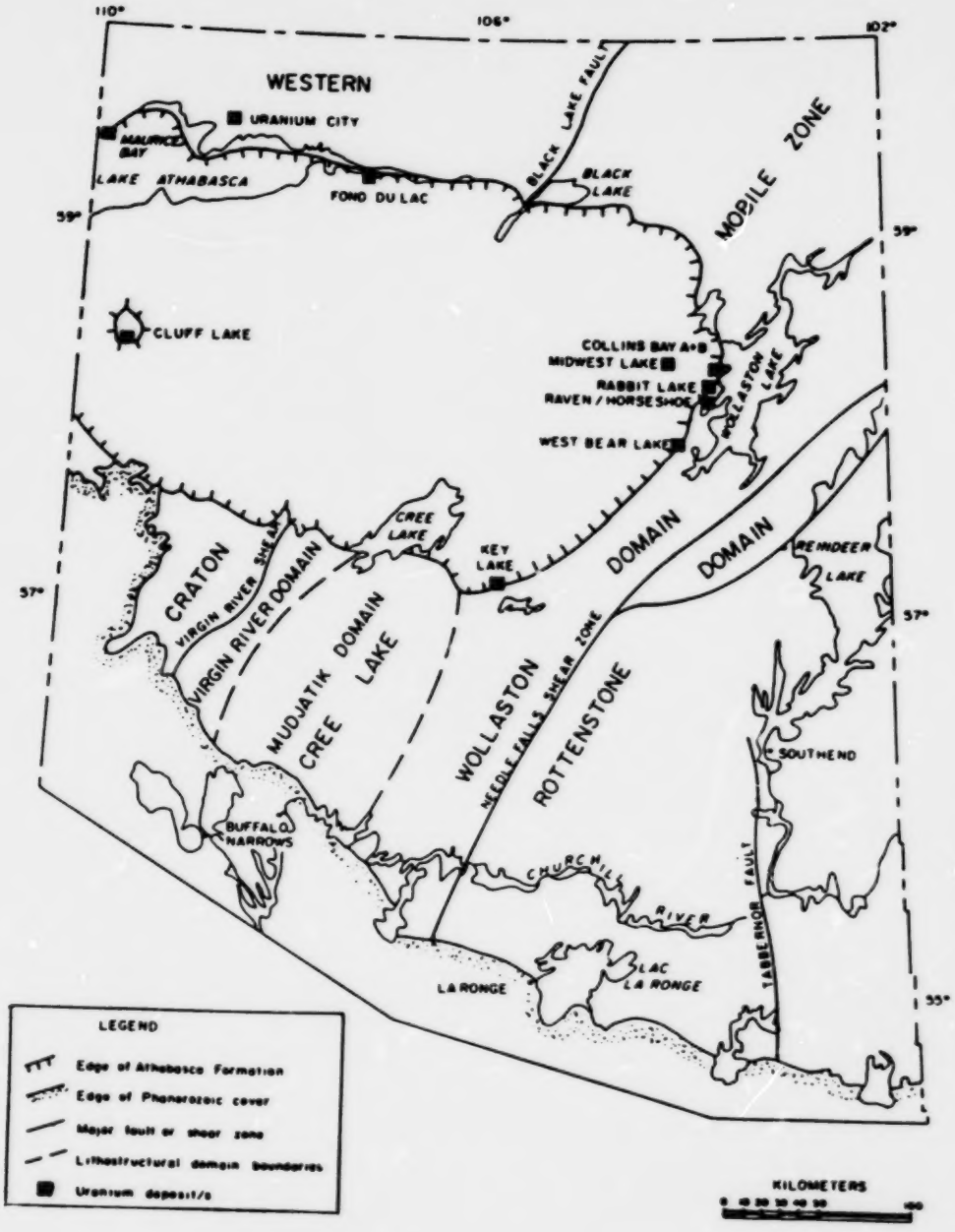


Figure 2.1: **Location Map of the Uranium Deposits in the Athabasca Formation, Saskatchewan (from Hoeve and Sibbald, 1978)**

most abundant nickel mineral followed by niccolite (NiAs) and bravoite ($(Ni,Fe)S_2$). Galena (PbS) of radiogenic origin is always present. Within the unaltered basement rocks pyrrhotite ($Fe_{1-x}S$) and chalcopyrite ($CuFeS_2$) have been observed. Extensive intergrowth of uranium and nickel minerals is present. Sooty pitchblende and coffinite can constitute the matrix for gersdorffite, millerite, niccolite and galena or vice versa.

Above the ore-bearing basement, uranium-nickel mineralization occurs intermittently in disseminated porous and fractured sandstone and conglomerate. Chlorite schist is the main uranium-nickel bearing host rock with quartzite host having a distinctly lower grade. In both the chlorite and quartzite hosts limonite ($FeO(OH).nH_2O$), hematite (Fe_2O_3) and carbonates ($(Ca,Mg)CO_3$) can accumulate in shear zones, cavities and fractures. Graphite (C) is present throughout the mineralization.

Collins Bay

The Collins Bay B-Zone uranium deposit, being mined by Eldor Mines, is situated on the west side of Wollaston Lake in northern Saskatchewan. The existing Rabbit Lake mill has been modified to enable processing of the Collins Bay ore which contains arsenic and nickel-bearing minerals.

The uranium mineralization in the B-Zone ore is made up of pitchblende (U_3O_8) and coffinite ($U(SiO_4)_{1-x}(OH)_{4x}$). Associated mineralization includes gersdorffite ($(Ni,Co)AsS$), skutterudite ($(Co,Ni)As_2$) niccolite (NiAs), millerite (NiS), galena (PbS), chalcopyrite ($CuFeS_2$) and pyrite (FeS_2). Elemental assemblages contain silver, arsenic, cobalt, chromium, copper, nickel, lead, titanium, vanadium and zirconium.

The Collins Bay A-Zone orebody contains pitchblende (U_3O_8) associated with rammelsbergite ($(Ni,Co,Fe)As_2$), pararammelsbergite ($NiAs_2$) and some galena (PbS) and sphalerite (ZnS).

The Eagle Point deposit, which forms part of the uranium ore reserves for the Eldor Mines operation, contains pitchblende (U_3O_8), coffinite ($U(SiO_4)_{1-x}$), uranophane ($Ca(UO_2)_2(SiO_3)_2(OH)_2.5H_2O$) and boltwoodite ($K_2(UO_2)(SiO_3)_2.5H_2O$). Associated minerals include gersdorffite ($(Ni,Co)AsS$), millerite (NiS), chalcocite (Cu_2S) and galena (PbS).

Cigar Lake

The Cigar Lake orebody is located approximately 115 km NE of the Key Lake Mine or 55 km WSW of Eldor Mines' operations at Rabbit Lake. The uranium in this high-grade deposit occurs as uraninite (UO_2) and pitchblende (U_3O_8) with coffinite ($U(SiO_4)_{1-x}(OH)_{4x}$) being present in smaller quantities. The sulfo-arsenides of nickel and cobalt can locally be major components of the ore with the main minerals being gersdorffite ((Ni,Co)AsS), skutterudite ($(Co,Ni)As_2$), niccolite (NiAs), bravoite ($(Ni,Fe)S_2$), cobaltite ((Co,Fe)AsS), and rammelsbergite ($(Ni,Co,Fe)As_2$). The sulfide minerals pyrite (FeS_2), marcasite (FeS_2), pyrrhotite ($Fe_{1-x}S$), smythite ($AgAsS_2$), chalcopyrite ($CuFeS_2$), covellite (CuS), bornite (Cu_5FeS_4), galena (PbS), jordisite (MoS_2), and sphalerite (ZnS) are also present in varying but generally smaller amounts.

Midwest Deposit

The Midwest uranium deposit is located northwest of the Rabbit Lake mine site near the eastern edge of the Athabasca Basin. The principal minerals in this deposit include pitchblende (U_3O_8), coffinite ($U(SiO_4)_{1-x}(OH)_{4x}$), gersdorffite ((Ni,Co)AsS), niccolite (NiAs), rammelsbergite ($(Ni,Co,Fe)As_2$). Also present are minor amounts of chalcopyrite ($CuFeS_2$), galena (PbS), bismuthinite (Bi_2S_3) polydimite (Ni_3S_4), and cobalt and silicate minerals. The pitchblende nickel-arsenide veins are associated with kaolinite-chlorite ($Al_4Si_4O_{10}(OH)_8$-$(Mg,Al,Fe)_{12}(Si,Al)_8O_{20}(OH)_{16}$) and sericite ($K_2Al_4Si_6Al_2O_{20}(OH,F)_4$).

Dawn Lake

The Dawn Lake deposit is also located northwest of the Rabbit Lake mine site. The Dawn Lake orebody is made up of several "pods" and hence the ore can be expected to vary in uranium grade and elemental assemblage. The mineralogy of the ore basically consists of pitchblende (U_3O_8), uraninite (UO_2) and coffinite ($U(SiO_4)_{1-x}(OH)_{4x}$) as uranium minerals with nickel arsenides, carbonates and goethite (FeO(OH)) being present as other constituents. Host minerals include quartz (SiO_2), chlorite ($(Mg,Al,Fe)_{12}$ $(Si,Al)_8O_{20}(OH)_{16}$), illite ($K_{1-1.5}Al_4Si_{7-6.5}Al_{1-1.5}O_{20}(OH)_4$), sericite ($K_2Al_4Si_6Al_2O_{20}$ $(OH,F)_4$) and titanium oxides (TiO_2).

McLean Lake

The McLean Lake deposit is located in close proximity to the Dawn Lake deposit northwest of the Rabbit Lake mine site. The McLean ore is made up of four facies.

The sulphide facies consists of bravoite-pyrite ($(Ni,Fe)S_2$-FeS_2), coffinite ($(SiO_4)_{1-x}(OH)_{4x}$), uraninite (UO_2), iron chlorite ($Fe_{12}(Si,Al)_8O_{20}(OH)_{16}$), illite ($K_{1-1.5}Al_4Si_{7-6.5}Al_{1-1.5}O_{20}(OH)_4$), siderite ($FeCO_3$) and chalcopyrite ($CuFeS_2$). The arsenide facies occur as arsenide-illite intergrowths, pararammelsbergite ($NiAs_2$), niccolite (NiAs), gersdorffite ((Ni,Co)AsS) and safflorite ($(Co,Fe,Ni)As_2$). A bleached facies contains nodular intergrowths of coffinite-pararammelsbergite and illite with subordinate nicollite, gersdorffite and arsenides. The oxide facies contains nodular intergrowths of coffinite-pararammelsbergite in hematized clay.

2.3 Elemental Composition of Ores

Typical analysis of Key Lake, Collins Bay B-Zone, Cigar Lake and Midwest ores are given in Tables 2-1, 2-2, 2-3 and 2-4 respectively.

For comparison, analyses of elements of concern to this study are provided in Table 2-5 along with typical analysis of Elliot Lake ore and Cluff Lake ore. The significant content of non-radionuclide contaminants in the norther Saskatchewan nickel-arsenide uranium ores associated with the Athabasca Basin is evident from a comparison of the values listed in this table.

2.4 Leaching Process

The leaching process for nickel-arsenic uranium ores is not significantly different from other uranium acid leaching circuits although relatively high acid concentrations must be maintained to ensure high uranium extraction and to stablize the leach liquor for preventing co-reprecipitation of uranium with other ions in solution. High oxidant addition is required in order to ensure oxidizing all uranium to the hexavalent state in the presence of the non-radionuclide contaminants in the ore.

TABLE 2.1: TYPICAL ANALYSIS OF KEY LAKE ORE

Element	Percent	
	Gaertner Ore	Deilmann Ore
U_3O_8	2.0	2.9
Ra-226	222 Bq/g	N/A
SiO_2	50	50
Fe	3.5	3.0
S	1.0	0.8
Cu	0.03	0.09
Zn	0.08	0.03
Mo	0.006	0.03
V	0.08	0.09
Ni	2.5	1.1
Co	0.08	0.08
Ti	0.4	0.6
Al	9.0	10.3
As	1.5	1.1
Ca	0.4	0.4
Mg	3.0	2.9
Na	0.7	0.9
K	0.6	1.5
F	0.05	N/A
P_2O_5	0.16	0.15
CO_2	1.0	0.8
Cl	0.05	N/A

TABLE 2.2: TYPICAL ANALYSIS OF COLLINS BAY B-ZONE ORE

Element	Percent
U_3O_8	0.6
ThO_2	0.003-0.04
Fe	1-3
S	0.1
Mo	0.01-0.02
V	0.02-0.05
Ni	0.4
As	0.5
PO_4	0.02
CO_2	0.2
Ra-226 (est)	60 Bq/g

TABLE 2.3: AVERAGE GRADE OF CIGAR LAKE ORE

Element	Percent
U_3O_8	14.5
Cu	0.7
Zn	0.04
Pb	1.2
Mo	0.14
Ni	1.0
Co	0.15
As	1.7
Ra-226 (est)	1,450 Bq/g

TABLE 2.4: AVERAGE GRADE OF MIDWEST ORE

Element	Percent
U_3O_8	2.2
Ra-226	275 Bq/g
L.O.I.	3.1
SiO_2	76
Fe	1.3
S	1.1
Cu	0.1
Zn	0.07
Mo	0.06
V	0.08
Ni	1.7
Co	0.2
Ti	0.3
Al	3.2
Mn	0.04
Cr	0.02
As	3.2
Ca	0.1
Mg	0.5
Na	0.1
K	1.2
F	0.05
P	0.03
CO_2	0.5
Cl	0.03
Zr	0.05
Rb	0.05
Sr	0.01

TABLE 2.5: COMPARISON OF SELECTED ELEMENTS IN VARIOUS URANIUM ORES

Ore	U_3O_8	Ni	As	Mo	Co	V
Key Lake (Gaertner)	2.0	2.5	1.5	0.006	0.08	0.08
Key Lake (Deilmann)	2.9	1.1	1.1	0.03	0.08	0.09
Collins Bay B-Zone	0.6	0.4	0.5	0.02	-	0.05
Cigar Lake	14.5	1.0	1.7	0.14	0.15	-
Midwest	2.2	1.7	3.2	0.06	0.2	0.08
Cluff Lake	0.7	0.003	0.001	0.02	-	0.02
Elliot Lake	0.1	0.003	L 0.005*	L 0.001	0.005	L 0.001

* L refers to "less than".

Acid leaching of the ground ore can be carried out in two stages, as practiced at Key Lake, or in a single stage as planned for the Collins Bay ore and as proposed for the Midwest ore.

Key Lake

At Key Lake the ore is ground in a SAG mill to a mesh-of-grind of minus 500 microns. The ground ore is dewatered in a thickener to a pulp density of 50% solids with the addition of a flocculant to assist in settling. The thickened pulp is then pumped to a two-stage leaching circuit where the ore is leached with sulphuric acid under oxidizing conditions. Typical leaching conditions for the two stages are given in Table 2.6. A two-stage circuit is used in order to recycle acid solutions for reducing overall acid consumptions and to prevent formation of ferric arsenate in the pregnant solution by providing reducing conditions for the ferric ion contained in the recycled acid solution.

The pulp first reports to the first-stage air-agitated pachucas where it is mixed with reclaimed acid solution (thickener overflow solution) from the second-stage leach and leached at atmospheric pressure and relatively low pulp density and temperature. Oxidant requirements in the first-stage leach are met by the injection of air used for agitation in the pachucas and the ferric content in the thickener overflow solution also acts as an oxidant for the leaching reactions. Acid requirements for the first-stage leach are met by the elevated acid level of the thickener overflow solution and by the addition of sulphuric acid as required.

The first-stage leach pulp is then pumped to the primary thickener where the thickener underflow is removed at 50% solids and pumped to the second-stage pressure leach feed tank. The overflow from the primary thickener is the pregnant solution which is pumped to solution pre-treatment ahead of the solvent extraction circuit.

Second-stage pressure leaching of the pre-leached ore slurry is carried out in a series of nine vertical pressure autoclaves. Sulphuric acid is added to the autoclave feed tank to provide the necessary acid levels for achieving high uranium extractions. Oxidant requirement is met by the injection of oxygen in the autoclaves. The second-stage leach slurry is then discharged into a surge tank for transfer to the eight stage counter-current-decantation (CCD) circuit.

TABLE 2.6: KEY LAKE LEACH CIRCUIT CONDITIONS

Data	First Stage	Second Stage
Particle Size (% - 74 microns)	50	50
Pressure (kPa)	atmospheric	600
Temperature (^{o}C)	25-30	60
Acid Concentration (g/L H_2SO_4)	12	40
Acid Consumption (kg/t H_2SO_4)	40	90
Pulp Density (% Solids)	15-20	50
Retention Time (h)	1	4

The overflow from the first-stage thickener in the CCD circuit is the acid solution recycled to the first-stage leaching step. Additional sulphuric acid is added in the CCD circuit in order to maintain adequate acid levels for preventing loss of uranium by reprecipitation. Minewater is used as wash water to effectively wash uranium-containing solution from the leached ore. The underflow from the last CCD thickener is pumped to the tails neutralization circuit.

Collins Bay

The Collins Bay nickel-arsenic uranium ore will be leached in the existing Rabbit Lake leaching circuit. In this circuit, ground ore is leached with sulphuric acid at 50°C under atmospheric pressure. Acidity levels in the leach are maintained at 30 g/L H_2SO_4. Sodium chlorate is added at a rate of approximately 7.5 kg/t $NaClO_3$ to maintain oxidizing conditions.

The leach slurry will then be pumped to the existing Rabbit Lake CCD circuit for recovery of pregnant solution. The washed leach residue will be pumped to the tailings neutralization circuit and the pregnant solution will be clarified prior to reporting to the solvent extraction circuit.

Midwest

Two different acid leaching circuits have been proposed for the Midwest ore, a single stage pressure leach and a single stage atmospheric leach with the use of two oxidants. Proposed leaching conditions for both options are listed in Table 2.7.

In the pressure leach alternative, ground ore at 30% minus 74 microns would be leached at 60°C with an oxygen over-pressure of 450 kPa for a period of 4 hours. Terminal acidities would be maintained at 50 g/L H_2SO_4 with the addition of sulphuric acid to the autoclave feed resulting in an acid consumption of 100 kg/t. Pregnant solution would be recovered from the leach slurry in an eight stage CCD circuit. Washed leach residue would be neutralized with lime for disposal to the tailings area. Pregnant solution would be clarified prior to pumping to the solvent extraction circuit.

TABLE 2.7: MIDWEST PROPOSED LEACH CIRCUIT CONDITIONS

Data	Pressure	Atmospheric
Particle Size (% - 200 mesh)	30	30
Pulp Density (% solids)	50	50
Temperature (^{o}C)	60	60
Pressure (kPa)	450	atmospheric
Time (h)	4	4
H_2SO_4 (kg/t)	100	80
Oxygen (kg/t)	20	-
Caro's Acid (kg/t)	-	29
$NaClO_3$ (kg/t)	-	5
Terminal Acidity (g/L)	50	50
Terminal emf (mV)	400 to 430	400

An atmospheric leaching circuit would leach the ore in air-agitated pachucas under atmospheric pressure maintaining acidity levels at 50 g/L H_2SO_4 with sulphuric acid. It has been proposed to supply oxidant requirements with Caro's Acid (H_2SO_5) formed on site by reacting hydgrogen peroxide with sulphuric acid. In order to maintain proper acidity levels it would be necessary to use a small amount of sodium chlorate as oxidant since usage of Caro's Acid alone would result in elevated acidity levels. The leach slurry would be processed as in the pressure leach option to recover pregnant solution.

2.4.1 Dissolution Characteristics

The dissolution characteristics of nickel, arsenic, molybdenum, cobalt and vanadium in uranium acid leaching circuits are dependent on the behaviour of their minerals in acid solution under oxidizing conditions. Typically for nickel-arsenic ores this infers a leach solution with acidity levels of 50 g/L H_2SO_4 and oxidation potentials of approximately 400 to 450 mV with solution temperature being 50-60°C.

Nickel-Arsenic

The chemistry occurring in the leaching of nickel-arsenic uranium ores has been previously identified in metallurgical studies on Key Lake ore. Nickel and arsenic dissolution is claimed to follow the general reactions:

$$2\ NiAsS_{(s)} + 6.5\ O_2 + 3\ H_2O \text{ ---- } 2\ Ni^{2+} + 2\ H_3AsO_4 + 2SO_4^{2-}$$
$$2\ NiAs_{(s)} + 4\ H^+ + 3.5\ O_2 + H_2O \text{ ---- } 2\ Ni^{2+} + 2\ H_3AsO_4^o$$
$$NiS_{(s)} + 2\ O_2 \text{ --- } Ni^{2+} + SO_4^{2-}$$

In the above reactions arsenides and sulphides are completely oxidized to arsenates and sulphates. It is not clear to what degree oxidation of the reduced minerals occurs in the mill.

It is possible to produce partial oxidation products such as $H_3AsO_3^o$ and S^o in solution.

Molybdenum-Cobalt-Vanadium

Molybdenum present in nickel-arsenidde uranimm ores mostly occurs as jordisite (MoS_2), an amorphous molybdenum sulphide, with minor occurrence of molybdenite (MoS_2).

Cobalt is associated with nickel in the nickel arsenide and nickel suphide minerals and also partially occurs as cobaltite ((Co,Fe)As S). Vanadium occurs as an amorphous, poorly crystallized, poorly defined compound. Typical reactions which can account for the partial dissolution of molybdenum and cobalt in an acid leaching circuit under oxidizing conditions would therefore be:

$$MoS_{2(s)} + 4.5O_2 + 3\,H_2O \rightarrow H_2MoO_4 + 4H^+ + 2SO_4^{2-}$$
$$2\,CoAsS_{(s)} + 6.5O_2 + 3\,H_2O \rightarrow 2\,Co^{2+} + 2\,H_3AsO_4^0 + 2SO_4^{2-}$$

Typical reactions for vanadium dissolution are not postulated since its mineral make-up has not been identified. However, after oxidation in an acid media the vanadium present in the ore will likely result as the oxide V_2O_5.

2.5 Mineralogy of Tailings

The mineralogy of the uranium tailings will significantly reflect the mineralogy of the original ore. However, many secondary minerals resulting from the mill process will be unique to the tailings. A mineralogical study of tailings from the Key Lake operation was reported by Knight and Piesold (1985). The information on uranium tailings containing significant amounts of As and Ni is limited to these data. A summary of the findings is given in Table 2.8. Arsenic and nickel occur both in their primary reduced forms (NiAsS, NiS, etc.) and in secondary precipitated form.

2.6 Arsenic and Nickel in Tailings Water

It is estimated that about 60% of the As and 55% of the Ni is leached from the primary ore minerals during milling (Neven et al., 1985) at Key Lake. These numbers are based on the results of analysis of total concentrations in the leaching solutions in the mill. The pregnant solution contains from 2.2 to 4.4 g/L of arsenic and 2.0 to 4.0 g/L of nickel. After extraction of uranium, the waste stream is neutralized in two stages, first at a pH of 6 to 7 and finally with lime to a pH greater than 11. After the first stage of neutralization, As levels are in the 2 to 3 mg/L range, while Ni occurs at concentrations of 10 to 20 mg/L. The second stage of neutralization reduces the As and Ni concentrations to 0.03 to 0.4 and 0.1 to 0.4 mg/L respectively.

TABLE 2.8: ESTIMATE OF MAJOR MINERALS FOUND IN KEY LAKE LAYERED URANIUM TAILINGS (from Knight and Piesold, 1985)

Mineral/Compound	Formula	Weight (%)
Major Constituents		
Quartz	SiO_2	48
Gypsum	$CaSO_4.2H_2O(2CaSO_4.H_2O)$	26
Graphite*	C	2
Illite, Trichlorite	(K, Al, Mg, Si, Ti, O, OH, Al, Mg, Si, O, OH)	7.4
Ettringite	$Ca_6Al_2(SO_4)_3(OH)_{12}.26H_2O$	3.7
Calcium Arsenate*	$Ca_3(AsO_4)_2.3H_2O$	2.0
Calcite*	$CaCO_3$	5.0
Gersdorffite	NiAsS	0.8
Nickel Compounds	NiS, $Ni(OH)_2$ Ni,FeS_2	2.0
Iron Compounds	Fe_2O_3,FeS_2,$Fe(OH)_3$	3.2
Minor Constituents		
Cobalt Compounds*	CoS,$Co(OH)_2$	0.1
Uranium Compounds	U(adsorbed), hydrated oxides	0.1
Zinc Compounds	ZnS, ZnFeS, $Zn(OH)_2$	0.1
Lead Compounds	PbS, $Pb(OH)_2$	0.1
Copper Compounds	CuS, $Cu(OH)_2$	0.1
TOTAL		100.2%

* Assumed, no measurements available.

Recent data showing arsenic and nickel concentrations in fresh discharge water, pore water, and seepage water from Key Lake tailings has been reported (Knight and Piesold, 1985). As and Ni data are summarized in Table 2.9. The fresh tailings refers to water discharged from the mill with the tailings solids. Pore water data represent samples of water extracted from the tailings. Seepage samples were collected from the sand under drain layer below the tailings. The leach samples refer to analysis of water used to leach portions of tailings solids in the laboratory.

TABLE 2.9: ARSENIC AND NICKEL CONCENTRATIONS IN DIFFERENT WATER SAMPLES ASSOCIATED WITH THE KEY LAKE TAILINGS
(Summarized from Knight and Piesold, 1985)

Water Type	As (mg/L)	Ni (mg/L)	No. of Samples
Fresh Tailings Discharge	0.76 to 4.6	0.011 to 0.29	4
Pore Water	0.37 to 13.0	0.041 to 0.56	13
Seepage	0.06 to 0.07	0.041 to 0.094	2
Leach Test	1.6 to 2.6	0.017 to 0.26	4

3.0 GEOCHEMICAL CONTROLS

Chemical substances are affected by numerous processes in aqueous systems that can enhance or limit concentrations in solution. Dissolution from solids, precipitation, adsorption on surfaces, complexation, redox transformations, degassing and, in some cases, biotransformation, can occur to substances in ground and surface water environments. Formation of a solid or adsorption on solid surfaces tends to limit concentrations in solution. Complexation results in concentrations that are higher than expected from some solubility limit. Redox transformation in solution will affect concentrations by altering the complexing, adsorption and solubility controls. These processes will be the focus of the following sections.

3.1 Arsenic

Lengthy reviews of arsenic geochemistry are available. These address aspects of worldwide arsenic distribution in rock types, mineral occurrences and general chemical behaviour (Onishi and Sandell, 1955; Baur and Onishi, 1978). Other reviews deal with the behaviour of arsenic in natural waters and address solubility controls, complexes, transformation processes and overall behaviour of this substance in its role as a potential contaminant (Ferguson and Gavis, 1972; Penrose, 1984; Lemmo et al., 1983). Although a mutlitude of studies have provided a vast quantity of information on arsenic behaviour in nature, there remain some basic unknowns in this highly scrutinized system. A brief review of arsenic behaviour is given below, followed by sections addressing the more detailed hydrochemical controls that are known or suspected.

Over 200 minerals containing arsenic in nature have been identified. Of these, almost one-half exist as arsenates (+5 oxidation state), one-quarter as sulphides and the remaining as oxides, silicates and in elemental form. Arsenopyrite is the most common mineral of arsenic with most of the arsenates and oxides resulting from oxidation of this and other sulphides and arsenides at the earth's surface. Arsenic in nature occurs primarily in the +3 and +5 oxidation states, but also exists in the -3 state in reduced organic compounds and rarely in the zero state as elemental arsenic.

A number of different secondary arsenic minerals have been identified in zones of weathered arsenide minerals. In one study of a weathered Pb-Zn-Ag deposit, three

arsenate minerals were identified in different zones (Taylor et al., 1984). Beudantite ($PbFe_3AsO_4SO_4(OH)_6$) was found in the sulphide zone. Mimetite ($Pb_5Cl(AsO_4)_3$) occurred in the oxidized zone that represents a transition between the fresh sulphide zone and the highly oxidized upper zone where hidalgoite ($PbAl_3AsO_4SO_4(OH)_6$) is common. Unfortunately, no solubility data are available for these minerals.

Reduced arsenic minerals such as arsenides or sulphides are generally unstable at the earth's surface. It may be possible to form simple sulphides in the presence of abundant hydrogen sulphide, but this has not been substantiated. Therefore, it is evident that reduced arsenic minerals are generally unstable and thermodynamic calculations of solubility have little meaning for their dissolution and oxidation. Solubility control by these types of solids is, therefore, not considered. Solubility control by other arsenites and arsenates was reviewed and calculations were performed to compare with available data.

A critical review of arsenic thermodynamic data was conducted, and a summary of the findings and appropriate constants are given in Appendix B.

3.1.1 Aqueous Complexes

Aqueous species in solution include the +3 and +5 oxidation states. The appropriate species and reactions are given in Table 3.1. When equilibrium is calculated in terms of pH and pE (or Eh), the dominant species in water are shown (Figure 3.1). In most natural waters (pH from 4 to 9), the dominant species will be $H_2AsO_4^-$ and $HAsO_4^{2-}$ in the +5 state and $H_3AsO_3^0$ in the +3 state. It is evident that the change in oxidation state will be important because of the different chemical behaviour expected between the anionic and the neutral charge species. Obviously, this will affect adsorption behaviour as shown by many studies (Gupta and Chen, 1978; Pierce and Moore, 1982) in which the trivalent form of arsenic was shown to be more mobile. Different solubility controls also apply to the two oxidation states with generally greater solubility attributed to the trivalent form.

One study (Cherry et al., 1979) has shown that arsenite (+3) will occur under moderately low redox conditions and that transformation between oxidation states in solution is kinetically favourable when low concentrations of naturally-occurring oxidants and reductants are present. The experimental data (Figure 3.2) show that arsenic (+3) is

TABLE 3.1: ARSENIC REACTIONS AND CORRESPONDING STABILITY CONSTANTS

	log K
Complexes	
$AsO_4^{3-} + H^+ \rightleftharpoons HAsO_4^{2-}$	+11.5
$AsO_4^{3-} + 2H^+ \rightleftharpoons H_2AsO_4^-$	+18.445
$AsO_4^{3-} + 3H^+ \rightleftharpoons H_3AsO_4^o$	+20.685
$HAsO_3^{2-} + H^+ \rightleftharpoons H_2AsO_3^-$	+12.11
$HAsO_3^{2-} + 2H^+ \rightleftharpoons H_3AsO_3^o$	+21.33
Redox	
$H_3AsO_3^o + H_2O \rightleftharpoons H_3AsO_4^o + 2H^+ + 2e^-$	-18.87
Solids	
$Ca_3(AsO_4)_2 \cdot 2H_2O + 6H^+ \rightleftharpoons 3Ca^{2+} + 2H_3AsO_4^o + 2H_2O$	-22.096

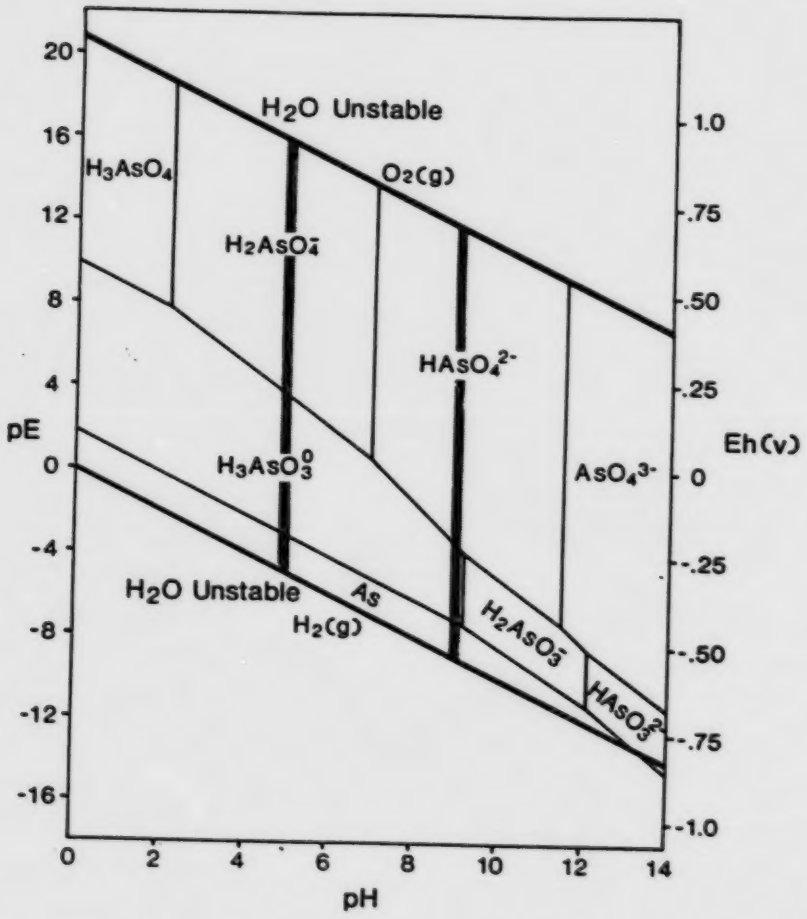


Figure 3.1: pE-pH Diagram for Arsenic in Water

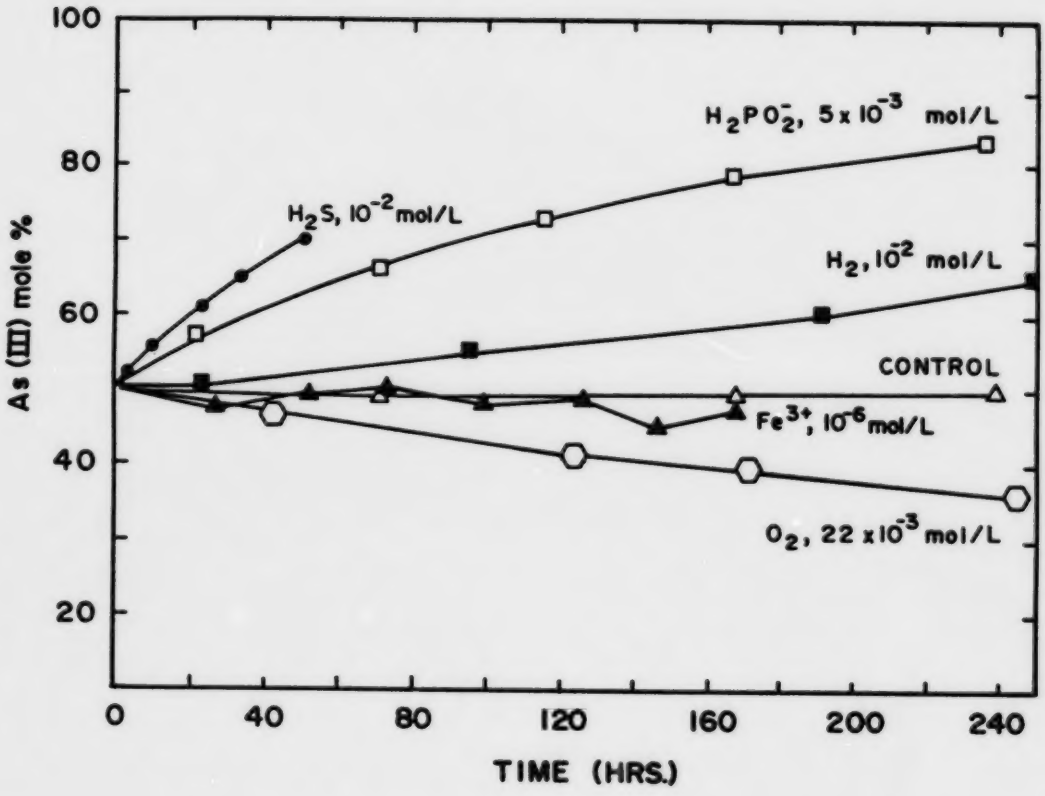


Figure 3.2: **Changes in As(+3) Concentration with Time Due to Oxidation or Reduction by the Substances Indicated**

oxidized and arsenic (+5) is reduced by appropriate substances in a measurable timeframe. The same study suggested that the arsenic redox couple (+3/+5) could be used as an indicator of redox conditions in groundwater systems because:

1. the couple was responsive, and
2. both members could be detected analytically at quite low concentrations.

A landfill leachate contaminated water did indeed show trends in the ratio of arsenite/arsenate in solution along the flow path that agreed with expected trends (Nicholson et al., 1983). Total arsenic levels were quite low, however, and the calculated redox condition (pE) was lower than that calculated or measured by other means. Nonetheless, arsenite is known to occur in groundwater, and it is likely that transformation of arsenate to arsenite can occur if a driving force for reduction such as oxidation of organic matter occurs in the groundwater system.

Pore water in lake bottom sediments that are rich in organics has been shown to have up to 90% of the total dissolved As in the monomethyl form (Holm et al., 1979). Evidence from experiments with other lake sediments suggests that oxidation of As(+3) occurs and may be related to manganese oxide coatings (Oscarson et al., 1980). These findings indicate that redox processes play an important role in arsenic mobilization and cycling in the environment.

Besides those forms of dissolved arsenic shown in the pE-pH diagram, there are no known complexes of importance in natural water. Using phosphate as an analogue for arsenate behaviour, there should be complexes involving cations, especially Ca^{2+}, such as $CaH_2AsO_4^+$ or $CaHAsO_4^o$. Preliminary findings by Gulens et al. (1979) suggest that strong complexes with Fe(III) occur, but no quantitative data were given. No reports were found to provide complexation data for arsenic species in solution.

3.1.2 Solubility Control by Solids

Numerous arsenate and arsenite solids have been prepared and studied. Much of the present information is based on early work conducted in the 1940's and 1950's (Chukhlantsev, 1956a, b, 1957), but more recent investigations have also addressed aspects of arsenic solubility especially with regard to metallurgical processes and discharge

control from mining operations (Heis and Blanchar, 1976; Robins, 1981; Krause and Ettel, 1985; Nishimura et al., 1985; Robins, 1985).

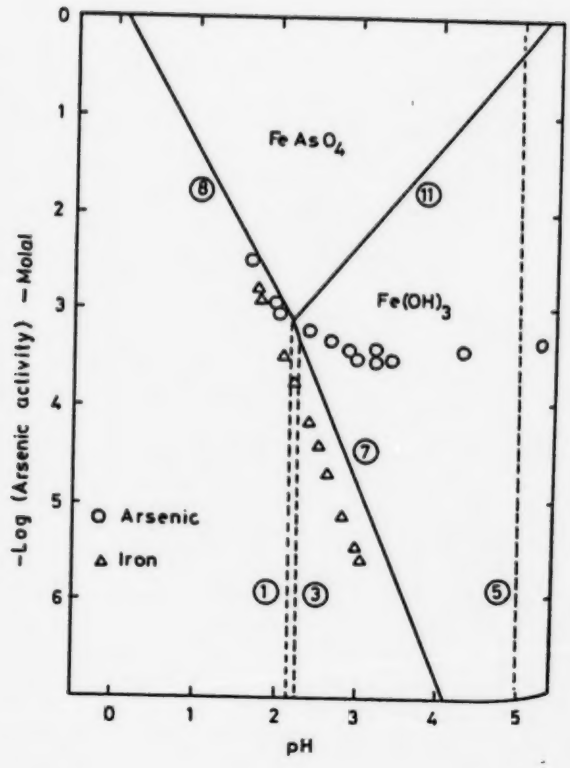
The solubilities of most arsenic solids range from many milligrams per litre of As to grams per litre in concentration. Examples of calculated arsenic concentrations as a function of pH are given by Robins (1983) for various solids (Figure 3.3). The solubilities of metal arsenites are almost without exception greater than those of the corresponding arsenates. The only solid which controls arsenic levels to mg/L levels is calcium orthoarsenate and then only at significantly elevated pH levels. The behaviour of calcium solids was studied in more detail.

There are reasonably good solubility and thermodynamic data available for calcium orthoarsenate. The solid has also been prepared and identified by x-ray diffraction methods (Nishimura et al., 1985). The solubility of As in equilibrium with this solid as a function of pH is shown in Figure 3.4. It is seen that As concentrations attain the mg/L level (10^{-4} mol/L) only when the pH is greater than about 11. Other calcium arsenate and arsenite solids have been formed and identified in experimental studies (Guerin, 1941, 1958; Nishimura et al., 1985). A summary of calcium arsenates is given in Table 3.2.

The thermodynamic data provided in Appendix B are given for the non-hydrated forms, but it is assumed that these solids represent the solid of that type regardless of hydration. This convention is used because hydration is highly dependent on temperature, and appropriate data were not available.

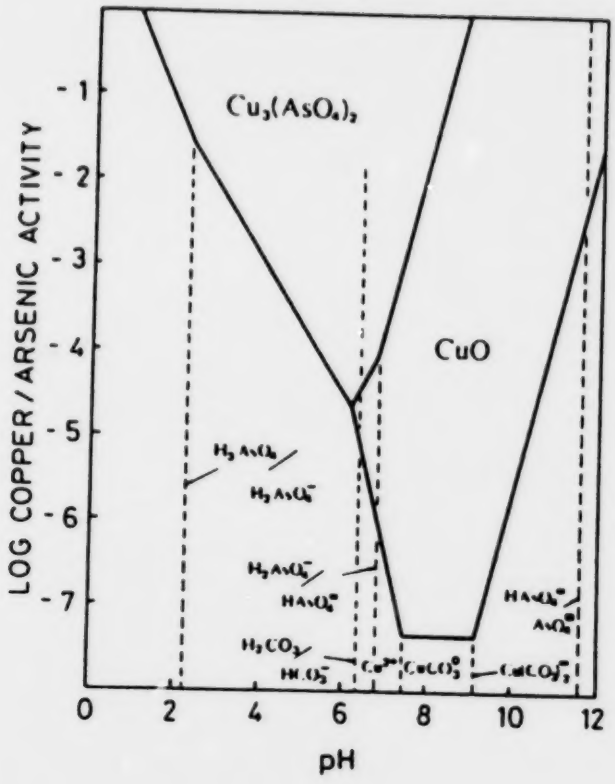
In any case, the solubilities of the calcium arsenates are all too high when the pH is below about ten to explain mg/L concentrations of As in tailings pore water, and hence other explanations are required for solubility controls.

Although there is no useful data to predict solubilities, experimental evidence suggests that some forms of ferric arsenate compounds may limit the solubility of arsenic over a broad range of pH values (Krause and Ettel, 1985). The study involved precipitation of ferric arsenate material under various conditions and in various sequence of reactant additions. The resulting solids were found to have variable molar ratios of Fe(III)/As(V). The solubility of these solids also varied with the molar ratio. The lowest arsenic concentrations in solution were observed when the solids were characterized by high



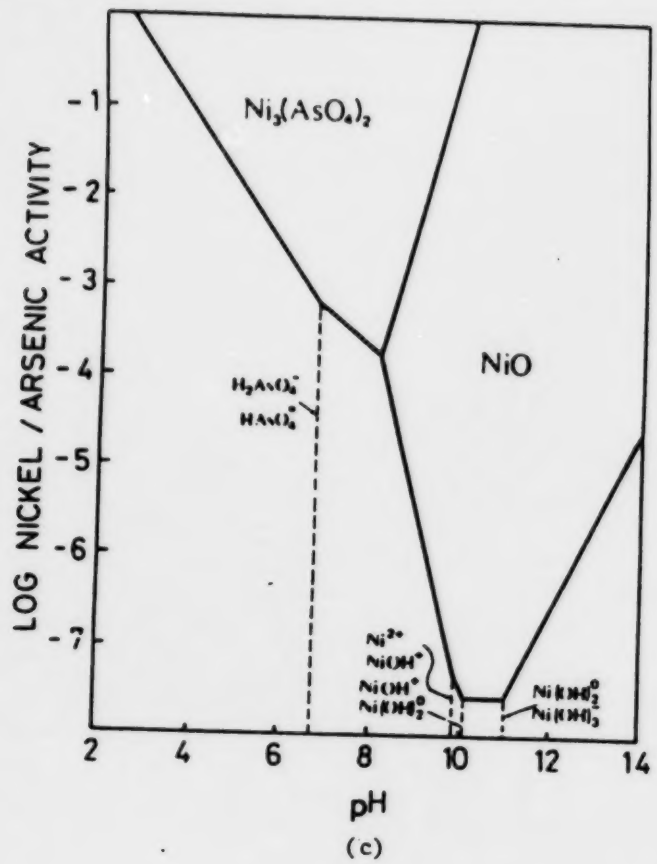
(a)

Figure 3.3: **Solubility of Various Metal Arsenates as a Function of pH: a) Ferric Iron; b) Copper; c) Nickel; d) Lead**



(b)

Figure 3.3: **Solubility of Various Metal Arsenates as a Function of pH: a) Ferric Iron; b) Copper; c) Nickel; d) Lead**



(c)

Figure 3.3: **Solubility of Various Metal Arsenates as a Function of pH: a) Ferric Iron; b) Copper; c) Nickel; d) Lead**

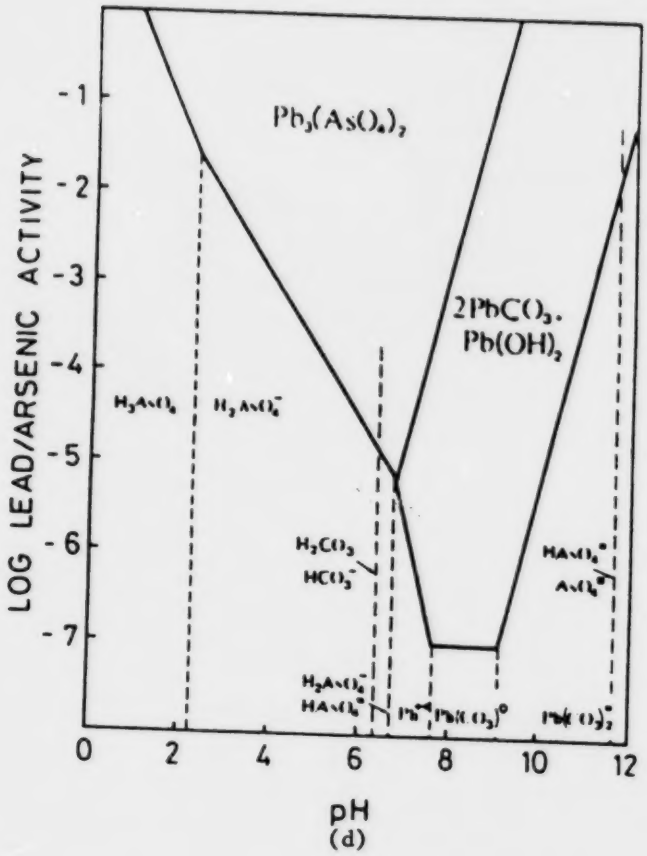


Figure 3.3: **Solubility of Various Metal Arsenates as a Function of pH: a) Ferric Iron; b) Copper; c) Nickel; d) Lead**

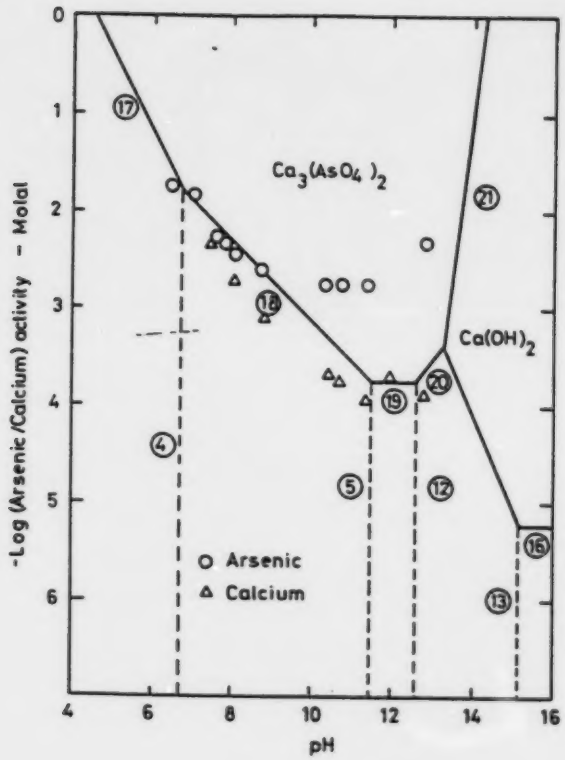


Figure 3.4: **Solubility of Calcium Orthoarsenate as a Function of pH**

TABLE 3.2: SOLIDS IN THE CALCIUM/ARSENIC(V)/WATER SYSTEM

Calcium Arsenate Formula	Equivalent Oxide Formula		Mineral Name	pH Range*
$CaH_4(AsO_4)_2$	$(CaO)_{1.0}(As_2O_5)_{1.0}(H_2O)_{2.0}$	(a,b,c)		2
$2\ CaHAsO_4$	$(CaO)_{2.0}(As_2O_5)_{1.0}(H_2O)_{1.0}$	(c)	Weilite	
$2\ CaHAsO_4 \cdot H_2O$	$(CaO)_{2.0}(As_2O_5)_{1.0}(H_2O)_{3.0}$	(a,b)	Haidingerite	5
$2\ CaHAsO_4 \cdot 2H_2O$	$(CaO)_{2.0}(As_2O_5)_{1.0}(H_2O)_{5.0}$	(a,b)	Pharmacolite	6
$2\ CaHAsO_4 \cdot 3H_2O$	$(CaO)_{2.0}(As_2O_5)_{1.0}(H_2O)_{7.0}$			
$0.5\ Ca_5H_2(AsO_4)_4$	$(CaO)_{2.5}(As_2O_5)_{1.0}(H_2O)_{0.5}$	(c)		
$0.5\ Ca_5H_2(AsO_4)_4 \cdot 4H_2O$	$(CaO)_{2.5}(As_2O_5)_{1.0}(H_2O)_{2.5}$	(b)	Sainfeldite	
$0.5\ Ca_5H_2(AsO_4)_4 \cdot 9H_2O$	$(CaO)_{2.5}(As_2O_5)_{1.0}(H_2O)_{5.0}$	(a)	Guerinite	7
$Ca_3(AsO_4)_2$	$(CaO)_{3.0}(As_2O_5)_{1.0}$	(c)		
$Ca_3(AsO_4)_2 \cdot 4H_2O$	$(CaO)_{3.0}(As_2O_5)_{1.0}(H_2O)_{4.0}$	(b)	Vladinairite	
$Ca_3(AsO_4)_2 \cdot 10H_2O$	$(CaO)_{3.0}(As_2O_5)_{1.0}(H_2O)_{10.0}$	(a)	Raienthalite	9
$Ca_3(AsO_4)_2 \cdot Ca(OH)_2$	$(CaO)_{4.0}(As_2O_5)_{1.0}(H_2O)_{1.0}$	(b,c)		
$Ca_3(AsO_4)_2 \cdot Ca(OH)_2 \cdot 4H_2O$	$(CaO)_{4.0}(As_2O_5)_{1.0}(H_2O)_{5.0}$	(a)		10

(a) Phases identified by Guerin (1941) at 17°C.

(b) Phases identified by Guerin (1941) at 40°C.

(c) Thermodynamic data given in Appendix B represent solid regardless of hydration.

* pH around which solid is stable as reported by Guerin (1941).

Fe/As ratios (up to 17) and the highest solubilities corresponded to the low Fe/As ratio solids (about 2). The solubility of arsenic as a function of pH for three different mole ratio solids is shown in Figure 3.5a. The corresponding solubility of ferric iron is shown as a function of pH in Figure 3.5b. Unfortunately, the reason for this behaviour is not understood. Neither is it clear why the molar ratios of the precipitated solids vary.

It is clear that the chemistry of metal-arsenate and arsenite solids is complex and that thermodynamic data are limited. A simple solid that controls arsenic concentrations to the low mg/L level at neutral pH levels has yet to be found and characterized. One solid that was postulated to provide such control was $Ba_3(AsO_4)_2$ for which some early experimental work indicated that the solubility product was quite low (Chukhlantsev, 1956a). These findings were reviewed by Robins (1985b) who showed that the original solubility data were in conflict with other earlier work (Guerin, 1938) and were probably in error as a result of measuring Ba rather than As concentrations, as well as extrapolation to higher pH values with little justification. Experimental work by Robins showed that barium arsenate solids were indeed more soluble than published values and the results of that work agreed well with that of Guerin. The solubility of barium arsenate solids is shown in Figure 3.6 in which comparison to earlier work is included. This example reinforces the concern of accepting thermodynamic data without question, even when these numbers appear in compiled sources that are usually reliable.

It is also known that the solubility of most arsenite (+3) minerals is quite high. Experimental studies (Guerin, 1958; Nishimura et al., 1985) showed that many arsenites, including those of Ca, Ba and Sr, have solubilities that result in arsenic concentrations in the mg/L range.

3.1.3 Adsorption Controls

In natural waters, arsenic occurs as an uncharged species ($H_3AsO_3^o$) in the +3 oxidation state and also as a mono- or divalent anion in the +5 oxidation state. Adsorption will, therefore, occur to a greater extent on positively charged surfaces that are associated with metal hydroxides. Adsorption of arsenic on alumina, bauxite, silica and carbon has been studied to determine removal characteristics in water treatment systems (Gupta and Chen, 1978). Adsorption onto aluminum hydroxide (Anderson and Malolky, 1979) and onto ferric hydroxides (Pierce and Moore, 1982) has been investigated to test adsorption

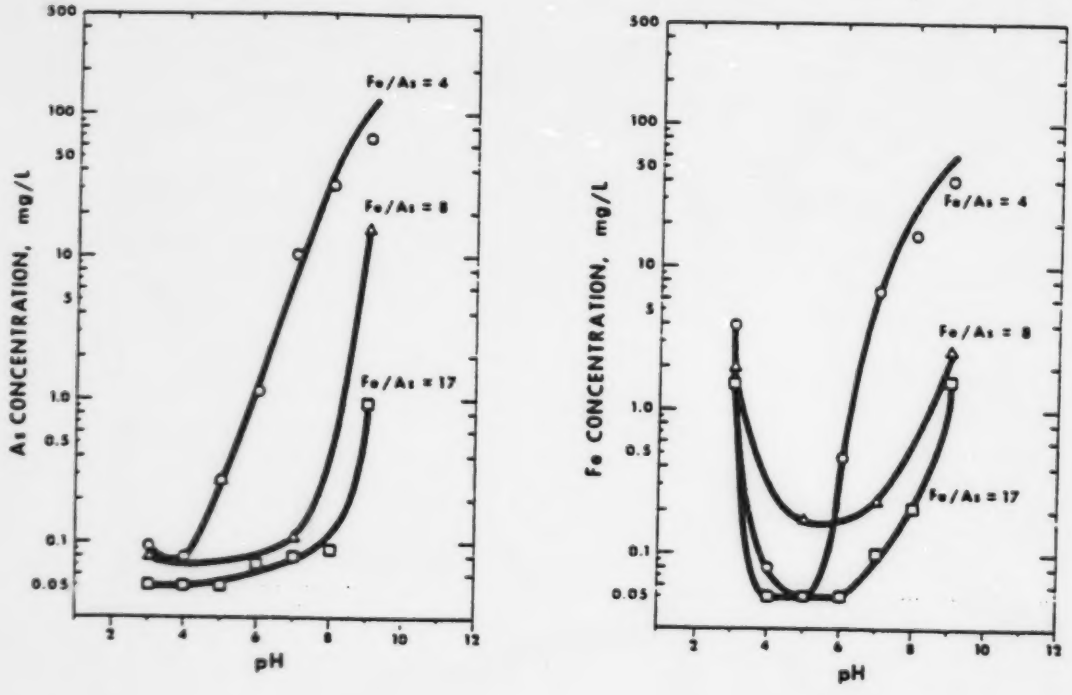


Figure 3.5: **Solubility of As(V) and Fe(III) as a Function of pH for Ferric Arsenate Solids with Different Mole Rations (from Krause and Ettel, 1985)**

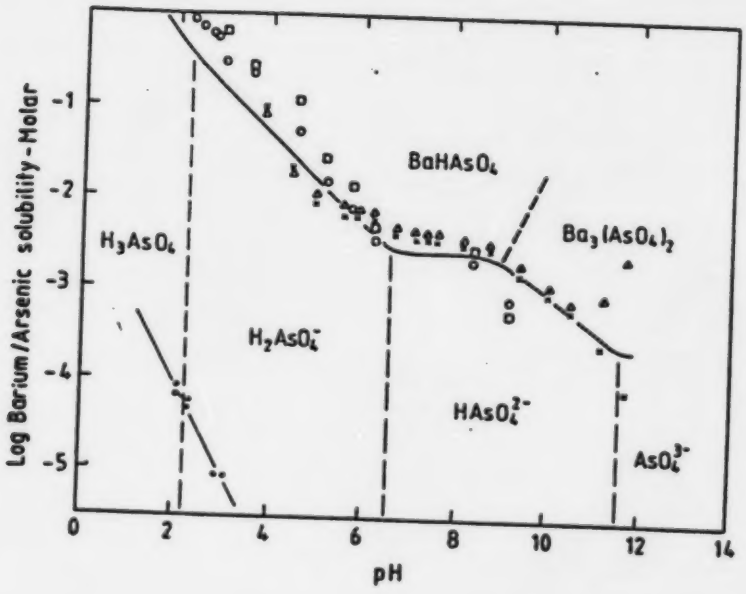


Figure 3.6: Solubility of Barium Arsenate Solids as a Function of pH (Robins' Data - Ba; triangles, As; X Guerin's data - Ba; O, As-squares Chukhlansev - Ba (only) closed circles, from Robins, 1985b)

models and to determine general adsorption behaviour. Arsenic also adsorbs onto clays as shown by experimental evidence in Frost and Griffin (1977). Other studies involving natural geologic sediments have also been conducted (Holm et al., 1979). More attention has been given to adsorption of phosphate which represents a reasonable analogue to arsenate (Parfitt, 1978). Although adsorption constants will not be the same for the two species, similar trends in behaviour are expected.

There are a number of ways in which adsorption has been modelled. A common approach for constant conditions and low concentrations of adsorbate is the Langmuir adsorption isotherm model. This model does not account for changes in pH or ionic strength. The K_d or linear adsorption approximation is based on this approach. Other models allow for surface complexation mechanisms that, to some extent, account for changes in solution chemistry and subsequent effects on the electrostatic nature of the solid surface. The constant capacitance model is one such method that includes the effects of pH but not of changing ionic strength. A more sophisticated approach called the triple layer model accounts for changes in both pH and ionic strength. However, increasing sophistication of the model used requires increased knowledge of the system that can usually be obtained only by experimental studies.

In general, arsenate adsorbs onto materials to a greater extent than does arsenite. The maximum adsorbance of arsenic on a number of solids is shown in Table 3.3. Adsorption of arsenite is less than that for arsenate by a factor of 3 to 5 in the examples given. It is also evident that aluminum and ferric hydroxide solids provide the most efficient adsorbents for arsenic.

3.1.4 Geochemical Model for Arsenic

Arsenic data that exist in the open literature have usually been collected for specific purposes, such as the study of concentrations in sediments or biota, or in water with little other chemical information included. Attempts to explain existing arsenic concentrations in surface or groundwater must address the complex interactions of the system including possible limitations in arsenic availability, precipitation or dissolution of solids and adsorption. Data from both laboratory and field studies were reviewed to determine environmental levels of arsenic in aqueous systems. Data related directly to arsenic in uranium tailings is presented by Knight and Piesold (1985) which shows that

TABLE 3.3: ADSORPTION DATA FOR ARSENIC

Adsorbate	Absorbed Mass (max.) (mmol/g)	Comments	Reference*
Alumina (act)	0.067 0.014	As(V) (As(III)	(1)
Bauxite (act)	0.052 0.016	As(V) As(III)	(1)
Carbon (act)	0.01	As(V)	(1)
Montmorillonite	(0.009)	As(V)	(2)
Kaolinite	(0.007)	As(V)	(2)
Ferric Hydroxide (am)	1.55 to 0.14 0.51	As(V) (pH = 4 to 9) As(III) (pH = 7)	(3)
Aluminum Hydroxide (am)	1.53	As(V) (pH = 4 to 8.5)	(4)
Sediments (anaerobic)	0.008	As(V)	(5)

* (1) - Gupta and Chen (1978)
(2) - Frost ;and Griffin (1977)
(3) - Pierce and Moore (1982)
(4) - Anderson and Malotky (1979)
(5) - Holm et al. (1979)

arsenic concentrations in tailings pore water is limited to a few mg/L or less. Other mine tailings data are given by Cherry et al. (1985) for a gold mine located in South Dakota. Arsenic levels in the pore water in that environment are limited to fractions of a mg/L even though sufficient arsenic exists in the tailings to provide much higher concentrations to the associated pore water. Other geochemical conditions are similar to those reported for Key Lake data in that gypsum is also present and pH occurs in the near-neutral range. Other data on arsenic concentrations exist. Low concentrations (sub ug/L levels) were reported by Nicholson et al. (1983) in landfill leachate contaminated groundwater. Groundwaters in North Dakota contained sub ug/L concentrations of arsenic (Nicholson, 1979, unpublished data). At the other extreme, arsenic concentrations in groundwater associated with gold, silver and cobalt mine wastes near Deloro, Ontario were in the range of 0.5 to 2.0 g/L (Bernard, 1983). Leachate discharging from uranium refinery wastes near Port Hope, Ontario was found to contain arsenic concentrations up to 2 mg/L (Hydrology Consultants Ltd., 1976).

The Key Lake data were chosen as the most appropriate to make comparisons with model results. Based on the concentrations of arsenic detected in tailings discharge and pore waters, thermodynamic data are not available for any solids to approximate the observed arsenic levels. One solid suggested in the report by Knight and Piesold (1985) is Haidingerite that is described therein by the formula $(CaO)_2.As_2O_5.3H_2O$. Other thermodynamic data suggest that the solubility of Haidingerite is actually an order of magnitude higher than that estimated in the above named report. It is stated in the report on Key Lake that the solubility constant used was derived in part from basic thermodynamic data (and probably from observed concentrations). The solubility of calcium orthoarsenate has also been invoked to predict arsenic concentrations, but solubility control is observed only at elevated pH.

The solubility limits for two solids are shown as a function of pH in Figure 3.7. The solids solubility compare favourably with the arsenic concentration observed at Key Lake. Unfortunately, there is no evidence for the dominant solid at neutral pH values. The solubility of this solid was taken from the Knight and Piesold report. One key feature of the data, however, is shown in this figure. It is evident that very little influence is exerted by pH on the total concentrations of arsenic. This phenomenon may be the result of geochemical mechanisms that are independent of pH. It is also possible that pH values are not quite representative of field conditions especially if pH values

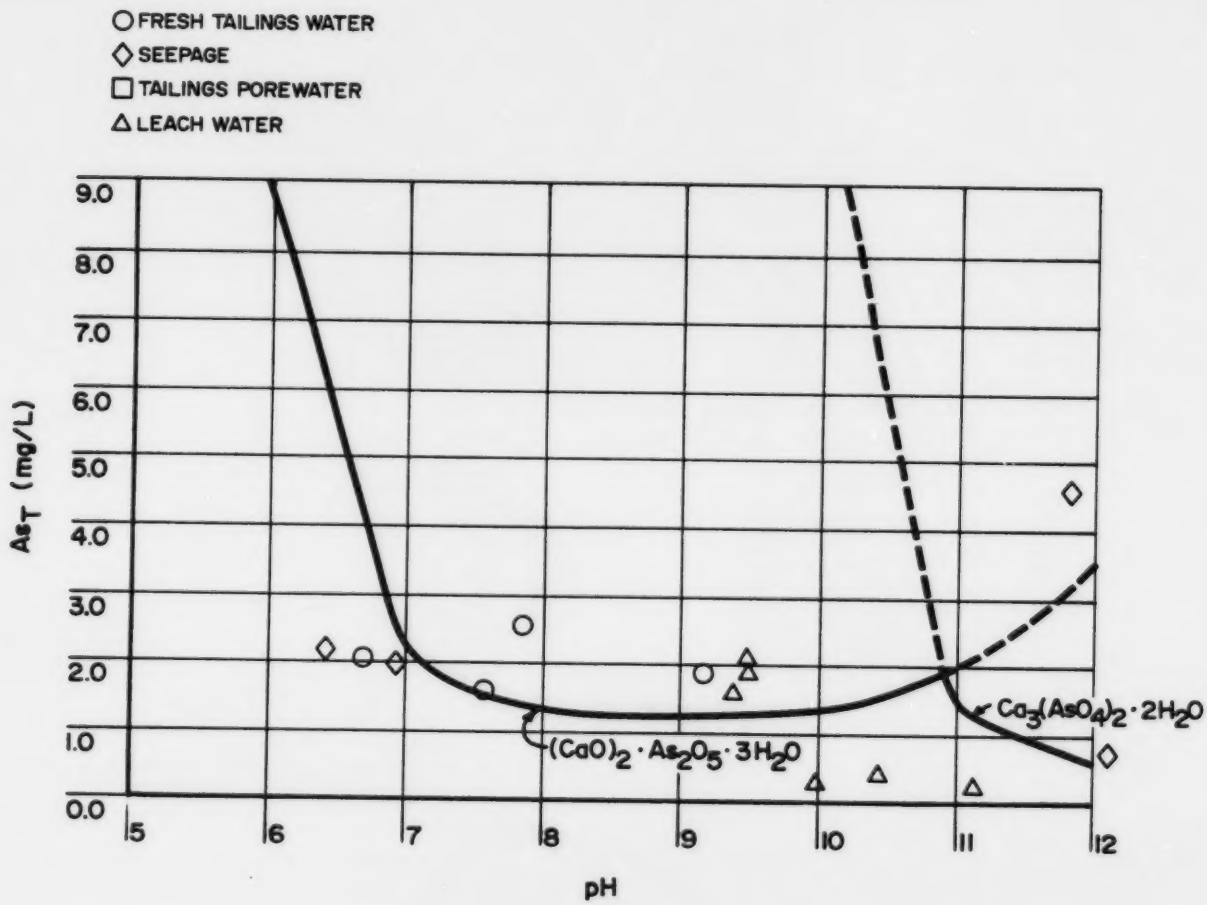


Figure 3.7: **Solubility Limits of Two Proposed Arsenate Solids as a Function of pH. Arsenic Concentration Data are from Knight and Piesold (1985)**

were measured only in laboratory. Changes in pH can occur due to degassing of CO_2 gas originally in the pore water or by precipitation of calcite that may have been induced during sample storage. Assuming that the observations are correct, however, requires that a mechanism that is relatively independent of pH in the range of 6 to 12 be involved.

As an alternative to control by solids, adsorption was investigated. Cherry et al. (1985) suggested that arsenic concentrations in the gold tailings pore water were controlled by adsorption on aluminum hydroxide coatings in the tailings. Adsorption constants based on independent laboratory experiments were used for model calculations. The constant capacitance model was used to simulate adsorption. The model resuults showed reasonably good agreement with observations. A similar approach was used here to model arsenic concentrations as a function of pH. The controlling equations with corresponding equilibrium constants are given in Table 3.4. The constants are the same as those used by Cherry et al. (1985) (Dzomok, pers. comm., 1986).

The effects of adsorption on arsenic (+5) concentration in solution (As_T) are shown in Figure 3.8 for changes in total available arsenic (As_{TT}) and total concentration of surface sites (X_T). The model results show that the concentration of arsenic is relatively insensitive to pH changes in the range of 5 to 10. This behaviour is consistent with the hypothesis that arsenate forms an inner sphere complex with the oxide surface sites and, therefore, is not greatly affected by protonation of the surface sites. When the concentration of surface sites is less than that of the total available arsenic, the concentration of arsenic in solution is constant. In other words, adsorption is only an important control of solution concentrations of arsenic when there are an excess number of sites. This will normally be the case in groundwater systems where ferric oxide coatings on mineral surfaces are common, and total available arsenic concentrations are generally low.

The total arsenic content was obtained from average values for the tailings reported by Knight and Piesold (1985) and assuming that 60% of the total arsenic is available for adsorption. In fully saturated tailings, the equivalent total arsenic (available for adsorption and dissolution) is 0.24 mol/L (18g/L). The total surface sites used were determined from the total estimated $Al(OH)_3$ and $Fe(OH)_3$, assuming that 60% of the total aluminum and 100% of the total iron in the tailings occur as the secondary hydroxides. Based on 1.5×10^{-3} mol/g of adsorption sites for the amorphous hydroxides

TABLE 3.4: ARSENIC ADSORPTION REACTIONS AND CORRESPONDING EQUILIBRIUM CONSTANTS THAT WERE USED BY CHERRY et al. (1985)

Equation			Log K
$XOH^{o} + 3H^{+} + AsO_4^{3-}$	$\rightleftharpoons$	$XH_2A\text{-}O_4^{o} + H_2O$	30.7
$XOH^{o} + 2H^{+} + AsO_4^{3-}$	$\rightleftharpoons$	$XHAsO_4^{-} + H_2O$	24.4
$XOH^{o} + H^{+} + AsO_4^{3-}$	$\rightleftharpoons$	$XAsO_4^{2-} + H_2O$	15.2
$XOH^{o} + 2H^{+} + SO_4^{2-}$	$\rightleftharpoons$	$XHSO_4^{o} + H_2O$	10.6
$XOH^{o} + H^{+} + SO_4^{2-}$	$\rightleftharpoons$	$XSO_4^{-} + H_2O$	6.2
$XOH^{o} + H^{+}$	$\rightleftharpoons$	XOH_2^{+}	7.0
XOH^{o}	$\rightleftharpoons$	$XO^{-} + H^{+}$	-12.99*

* This value is from Anderson and Malotky (1979) for $Fe(OH)_3$.

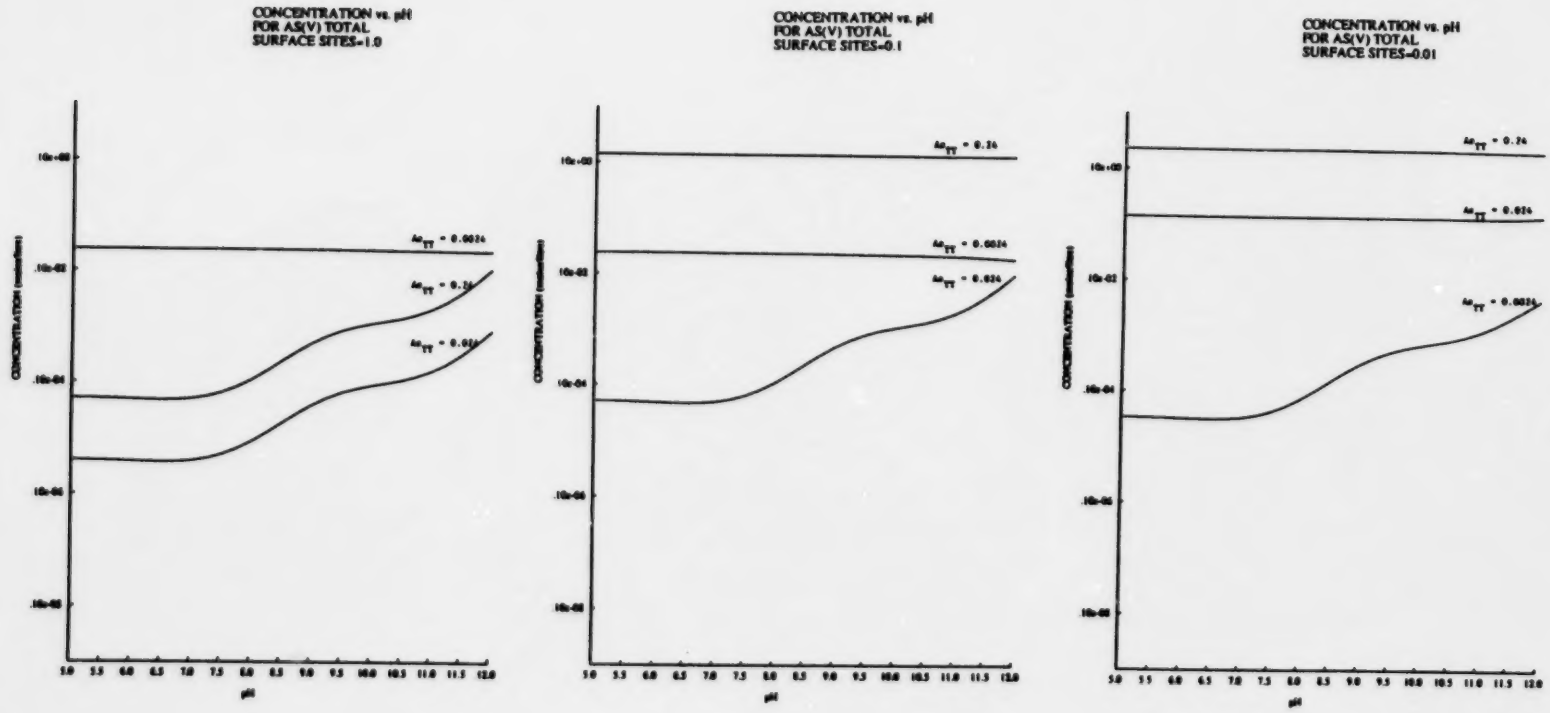


Figure 3.8: Arsenic in Solution Versus pH for the Adsorption Model with Different Values of Total Available Arsenic (As_{TT}) and Surface Sites (X_T)

(Anderson and Malotky, 1979), the equivalent concentration of surface sites in completely saturated tailings is about 0.6 mol/L. The model results reflect the data and show very little effect of pH under the conditions used (Figure 3.9). Because of the empirical nature of some of the equilibrium constants used, these results should not be accepted without question. In addition, the log scale for arsenic concentrations tends to reduce the apparent variability of the arsenic concentrations, as well as the deviation between data and model results. The results do, however, give support to the hypothesis that adsorption can control arsenic concentrations in the tailings. The fact that protonation constants and adsorption constants for the various sites were chosen independently of the observed data also provides evidence for control by this mechanism.

This model is not definitive. More complex reactions will occur due to the presence of ferric hydroxide that will also adsorb arsenic. This evidence, however, in addition to other independent evidence of arsenic adsorption suggests that this is a likely mechanism to control arsenic concentrations in the tailings pore water.

The detailed studies of the calcium-arsenate system conducted by Nishimura et al. (1985) shows that arsenic concentrations fall below the mg/L level only when the pH rises above about ten when calcium solids are involved. Although thermodynamic data were not determined in that study, the calcium arsenate solids were well characterized. The results provide strong evidence that calcium solids do not provide the required limit on arsenic solubility. The investigation of ferric arsenate solubility by Krause and Ettel (1985) does show that some uncharacterized solids containing ferric iron and arsenate are capable of limiting arsenic to sub mg/L levels even at pH levels between 3 and 9. The results of the experiments reported leave some question to whether or not arsenic adsorption is also involved, as well as precipitation of ferric arsenate solids. This question is analogous to the uncertainty involved in phosphate removal by ferric iron flocculation. That is, whether ferric phosphate forms and settles out, or whether ferric hydroxide precipitation provides highly active adsorption sites for phosphate. It would seem that the key to low arsenic concentrations centre on ferric iron for potential solid formation and adsorption control. This area of uncertainty is worthy of further investigation.

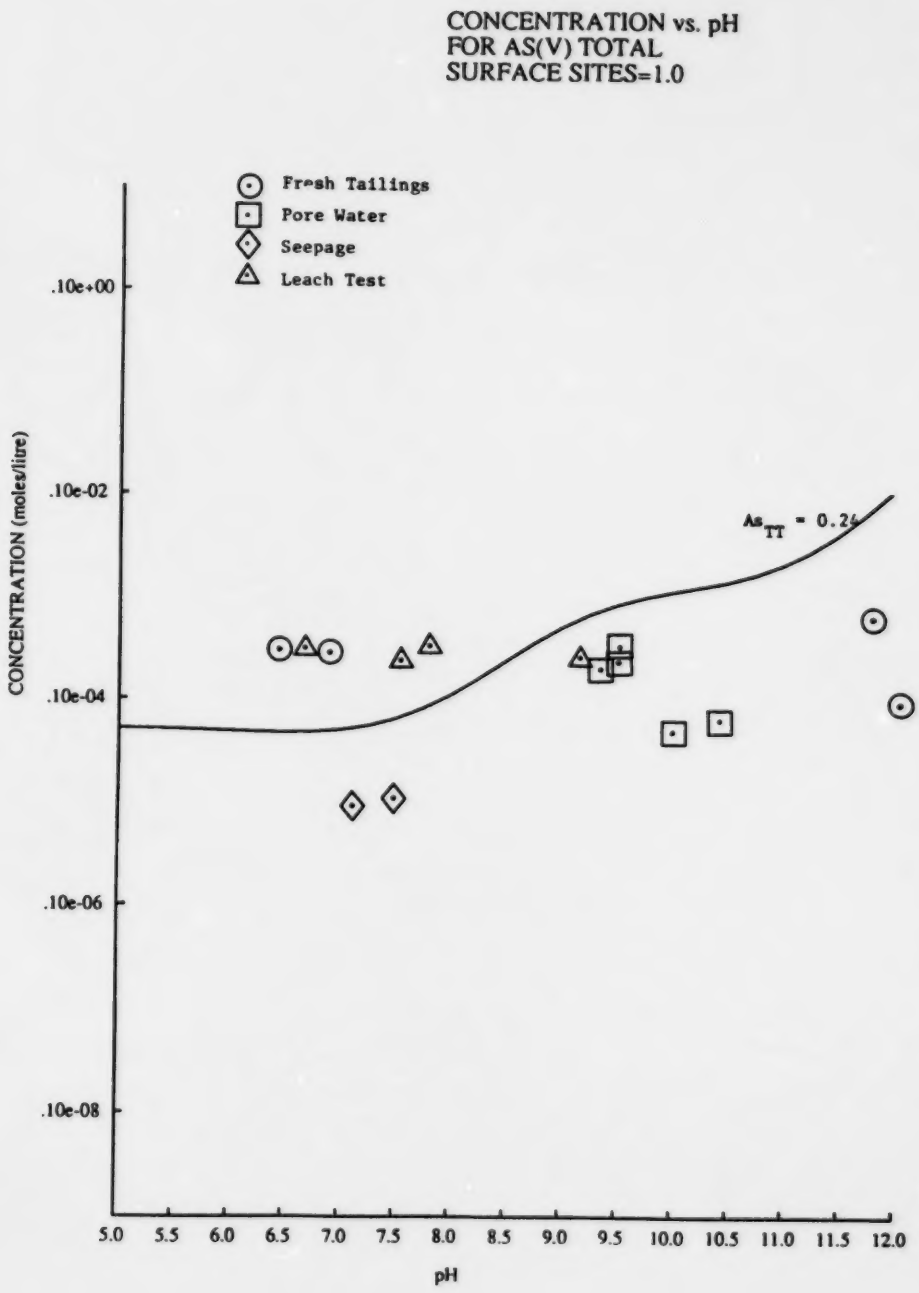


Figure 3.9: **Adsorption Model Results for Arsenic Compared to Key Lake Arsenic Data. Appropriate surface site and total available arsenic concentrations were used as input parameters.**

3.2 Nickel

Nickel occurs in many mineral forms in nature. Only the Ni(+2) oxidation state exists under natural conditions. Reviews of nickel in the environment have been compiled in one volume (Nriagu, 1980) and nickel has received attention by geologists for its role in oxidized enriched ore zone ("supergene ores") development (Thornber, 1975a, b; Taylor et al., 1984). The association of high nickel concentrations in uranium ore in the Athabasca Basin, Saskatchewan has been studied (Hoeve and Sibbald, 1978).

The primary ore mineral of nickel, worldwide, is pentlandite ($(Fe,Ni)_9S_8$) with other important reduced minerals consisting of niccolite (NiAs), breithauptite (NiSb), millerite (NiS), rammelsbergite $(Ni,Co)As_2$), gersdorffite ((Ni,Fe,Co)AsS) and ullmanite (Ni,SbS). Nickel is known to occur in geothite and other ferric oxide minerals formed by leaching and subsequent precipitation. During weathering, nickel is known to precipitate as complex hydrous silicates with layer lattices. Important secondary nickel minerals include annabergite ($(Ni,Co)_3(AsO_4)_2 \cdot 2H_2O$), garnierite ($(Ni,Mg)_3Si_2O_5(OH)_4$), neponite (nickeliferous chlorite) and pimelite ($(Ni,Mg)_3Si_4O_{10}(OH)_2$). Other compounds of sulphates, chlorides, nitrates, carbonates, oxides, hydroxide and organic complexes are also possible. The aqueous chemistry is dominated by hydrolysis, but other complexing species are also important in natural systems.

3.2.1 Aqueous Complexes

The most important complexes formed in aqueous systems and their corresponding stability constants are given in Table 3.5. The hydrolysis of nickel occurs, to a significant degree, above pH values of about 8. The $Ni(OH)_2^0$ species dominates between pH values of about 9 and 11, while the $Ni(OH)_3^-$ species is most significant between pH values of 11 and 13 in relatively dilute solutions containing nickel. Of the other complexes that are important in natural aqueous systems, $NiSO_4^0$ and $NiCO_3^0$ are the most significant. When nickel activities are controlled by equilibrium with a solid (i.e., $Ni(OH)_2$), these complexes can each effectively double the total nickel concentrations in solution compared to values if SO_4^{2-} or CO_3^{2-} were not present. The other complexes consisting of $NiCl^+$ and $NiHCO_3^+$ can also be important under certain conditions.

TABLE 3.5: NICKEL REACTIONS AND CORRESPONDING STABILITY CONSTANTS

		log K
Hydrolysis Complexes		
$Ni^{2+} + H_2O$	$\rightleftharpoons NiOH^+ + H^+$	-9.86
$Ni^{2+} + 2H_2O$	$\rightleftharpoons Ni(OH)_2^o + 2H^+$	-20.28
$Ni^{2+} + 3H_2O$	$\rightleftharpoons Ni(OH)_3^- + 3H^+$	-29.05
$Ni^{2+} + 4H_2O$	$\rightleftharpoons Ni(OH)_4^{2-} + 4H^+$	-44.0
$4Ni^{2+} + 4H_2O$	$\rightleftharpoons Ni_4(OH)_4^{4+} + 4H^+$	-27.71
Other Complexes		
$Ni^{2+} + Cl^-$	$\rightleftharpoons NiCl^+$	+0.747
$Ni^{2+} + SO_4^{2-}$	$\rightleftharpoons NiSO_4^o$	+2.31
$Ni^{2+} + CO_3^{2-}$	$\rightleftharpoons NiCO_3^o$	+5.35
$Ni^{2+} + HCO_3^-$	$\rightleftharpoons NiHCO_3^+$	+2.2
Solids		
$Ni(OH)_2$ (alpha) + $2H^+$	$\rightleftharpoons Ni^{2+} + 2H_2O$	+15.03
$Ni(OH)_2$ (beta) + $2H^+$	$\rightleftharpoons Ni^{2+} + 2H_2O$	+10.81
$NiFe_2O_4$ (s) + $2H^+ + 2H_2O$	$\rightleftharpoons Fe(OH)_3$ (am) + Ni^{2+}	+0.105
$NiFe_2O_4$ (s) + $2H^+$	$\rightleftharpoons FeOOH(s) + Ni^{2+}$	+9.64
NiS(s)	$\rightleftharpoons Ni^{2+} + S^{2-}$	-22.9

3.2.2 Solubility Control by Solids

There is evidence in nature that nickel concentrates in specific zones that are exposed to weathering. In the development of supergene enriched ores near the earth's surface, nickel is one of the final metals to be leached from the oxidized sulphide zones. The presence of nickel latterites, or ores that are composed predominantly of aluminum oxides after severe weathering, suggests that nickel mobility can be quite restricted by secondary solids. Over shorter time periods, there is strong evidence that $Ni(OH)_2$ solid controls nickel activities in solution (Baes and Mesmer, 1976). There has been much effort extended to quantify the solubility product of this solid. Early work in this area identified the presence of a solid with variable stability. A relatively stable aged solid referred to as beta-$Ni(OH)_2$ represents the lower solubility limit (see Table 3.5). At the other end of stability range is the freshly precipitated material referred to as alpha-$Ni(OH)_2$ that represents the upper solubility limit. More recent studies give support to the variable stability claim (Novak-Adamic et al., 1973). In this way, nickel is not unlike ferric iron for which hydroxide solids of varying stability have also been recognized. The solubility of beta-$Ni(OH)_2$ is shown in Figure 3.10 with the contributions by individual nickel species and complexes.

This phenomenon provides some degree of difficulty in predicting nickel concentrations in solution. When this solid is suspected, the precise solubility constant will be unknown and, therefore, it is difficult to precisely predict the resulting nickel activity set by the solid. Alternatively, if some data are available to provide an indication of the nickel hydroxide solubility, then it may be possible to use these data for further calculation under subsequent conditions with that solid.

Most other solid salts of nickel are quite soluble. Calculations involving solubility data for many sulphates, a carbonate, arsenate and mixed hydroxy-sulphates indicate that nickel concentrations would extend to tens, hundreds and even thousands of mg/L across most of the pH range. There is one other solid phase that may provide sufficient solubility control to limit nickel concentrations to low mg/L levels. Nickel ferrite ($NiFe_2O_4$) has been hypothesized to exist and to control nickel levels in soil systems (Hem, 1977; Sadiq and Enfield, 1984a, b). The activity of nickel resulting from nickel-ferrite equilibrium depends on the activity of ferric iron in solution. Because the ferric iron is generally controlled by some form of ferric hydroxide solid that can have a

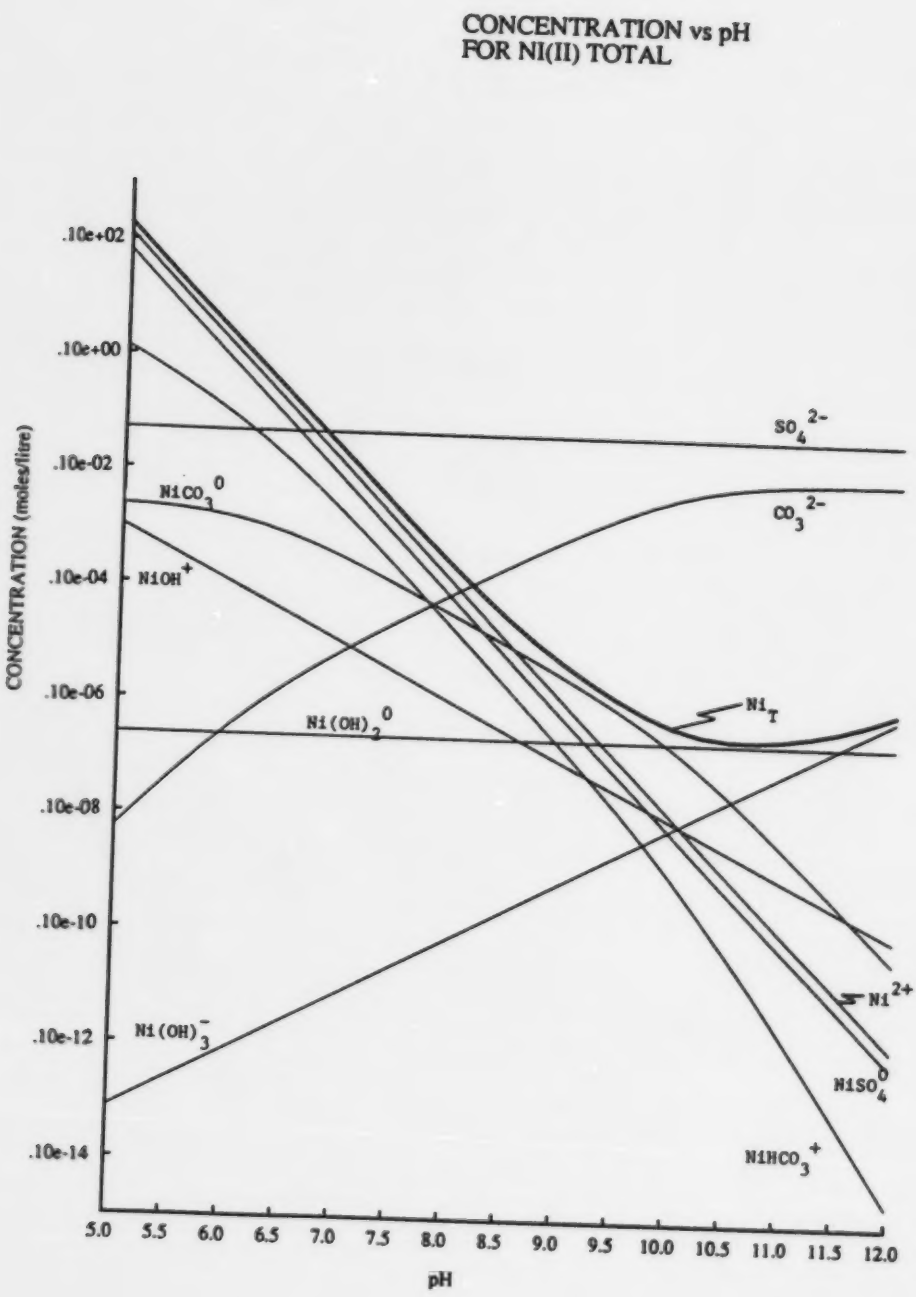


Figure 3.10: **Solubility of Nickel as a Function of pH in Solution with Beta-$Ni(OH)_2$. Aqueous complexes are given for conditions of gypsum saturation controlling SO_4^{2-} concentrations and total dissolved carbonate concentrations of 10^{-3} mol/L.**

variable stability constant, the nickel activities controlled by nickel-ferrite can also vary (see Table 3.5). The results of laboratory experiments by Sadiq and Enfield involving nickel addition to 21 different soil suspensions provide strong evidence for nickel ferrite control. Presumably, the soil types used reflect a wide variety of materials, in addition to spanning pH values over about two units. The authors recognized that the results do not match exactly the theoretical solubility product but the variable ferric hydroxide solid could easily account for the consistent discrepancy. The correlation of iron and nickel in terrestrial derived sediments in the ocean also provides support for this control on nickel concentrations (Trefry and Presley, 1976). In reducing environments such as organic-rich lake sediments or some groundwaters, nickel sulphide could provide a control on nickel concentrations in the associated pore water. Unless there is sufficient organic material to generate sulphide, this solid phase is not likely to be important.

3.2.3 Adsorption Controls

When nickel is abundant in a specific environment, control of solubility by precipitation of solids is quite likely. In other environments, the correlation of nickel content with clay content in lake sediments (Fitchko and Hutchinson, 1973) and with particulate surface area (Oliver, 1973), as well as with hydrous ferric and manganese oxide contents (Frefry and Presley, 1976) supports the hypothesis of adsorption control of nickel. Jenne (1968), in a review of possible controls on nickel, concluded that adsorption on hydrous manganese and iron oxides provide the principal control on nickel concentrations in soils and surface water with suspended matter.

Nickel adsorption on various solid surfaces has also been investigated experimentally. Adsorption onto manganese and iron oxides indicated that nickel has one of the lowest affinities for adsorption compared with Pb, Cu, Mn, Co and Zn (McKenzie, 1980). Similar results were observed by Harter (1983) in a study involving various soil samples as adsorbates. The results of that investigation showed that nickel was retained strongly, with less than 50% of the sorbed nickel released in 0.01 M HCl for "adsorption" at pH = 8 and above. The original concentrations of nickel added to the soil suspensions were less than those that would induce precipitation of $Ni(OH)_2$ solid, but formation of other solids were not ruled out. Saurez and Langmuir (1976) found a strong correlation between manganese and nickel in soils affected by landfill leachate. Manganese oxides were found to occur as coatings on quartz grains. Adsorption of nickel on precipitated silica

(Bye et al., 1983) revealed that the series for adsorption affinity in descending order was Cu, Zn, Cd, Co and Ni. Adsorption by MnO_2 also showed that nickel had the lowest affinity for the surface sites with the affinity series in descending order of Mn, Zn, Cd, Co and Ni (Gray and Malati, 1979). Adsorption on clays has also been studied for exchange reactions with K^+ and Ca^{2+} (Bansal, 1982). Nickel is the preferred ion on the exchange site compared to both of these competing ions.

An experimental study that also included equilibrium modelling of nickel adsorption onto various solids was reported by Theis and Richter (1980). Hydrolysis and aqueous complex formation were accounted for in the modelling approach. The results showed that significant adsorption onto geothite was achieved above a pH of 5.5, while adsorption on silica occurred above a pH of 6.5. Experimental results compared favourably with model behaviour even when complexing agents were used to modify the adsorption characteristics.

3.2.4 Geochemical Model

The review of nickel geochemistry shows that evidence exists for both the simple hydroxide solid and nickel ferrite controls of nickel concentrations in aqueous systems. In addition, adsorption onto ferric iron and manganese oxides and other solids likely controls nickel levels in many environments. The combination of these controls can complicate the modelling of the nickel system.

The nickel concentrations associated with the Key Lake tailings are plotted in Figure 3.11. The solubility of beta-$Ni(OH)_2$ is shown as a function of pH. The solubility shown here has included in it the effect of hydrolysis and complexes of sulphate and carbonate, the concentrations of which were set at values similar to those found in the tailings. Nickel concentrations in the fresh tailings discharge and seepage agree fairly well with the solubility of $Ni(OH)_2$. It should be noted that control of nickel concentrations by nickel ferrite (also shown in Figure 3.11) results in behaviour that is similar to that exerted by $Ni(OH)_2$ when the ferric oxide is represented by goethite (FeOOH). These similarities make it difficult to distinguish the effects of one or the other of the solids. Nickel ferrite solubility is much lower if equilibrium with amorphous ferric hydroxide is assumed (Figure 3.11, lowest curve). The existence of nickel ferrite has not been shown directly, but is based on inferences from ion activity product data in experimental

studies. Also included in Figure 3.11 for comparison is the solubility of the most stable nickel sulphate solid. It is obvious that this solid is far too soluble to provide reasonable limits on nickel concentrations in solution.

The remaining data representing concentrations in the tailings pore water and the laboratory leach water appear to be insensitive to pH levels.

An adsorption model (constant capicitance) was developed and tested to determine the response of nickel concentrations to changes in pH. An estimate of the primary adsorption constant was made because no data were available in the literature. The model results of total dissolved nickel are shown for different values of total available nickel (Ni_{TT}) and surface sites (X_T) in Figure 3.12. The shape of the curves is similar to those when $Ni(OH)_2$ solid controls solubility. There is no evidence to suggest that the adsorption model describes the experimental data better than solubility control by the hydroxide solid.

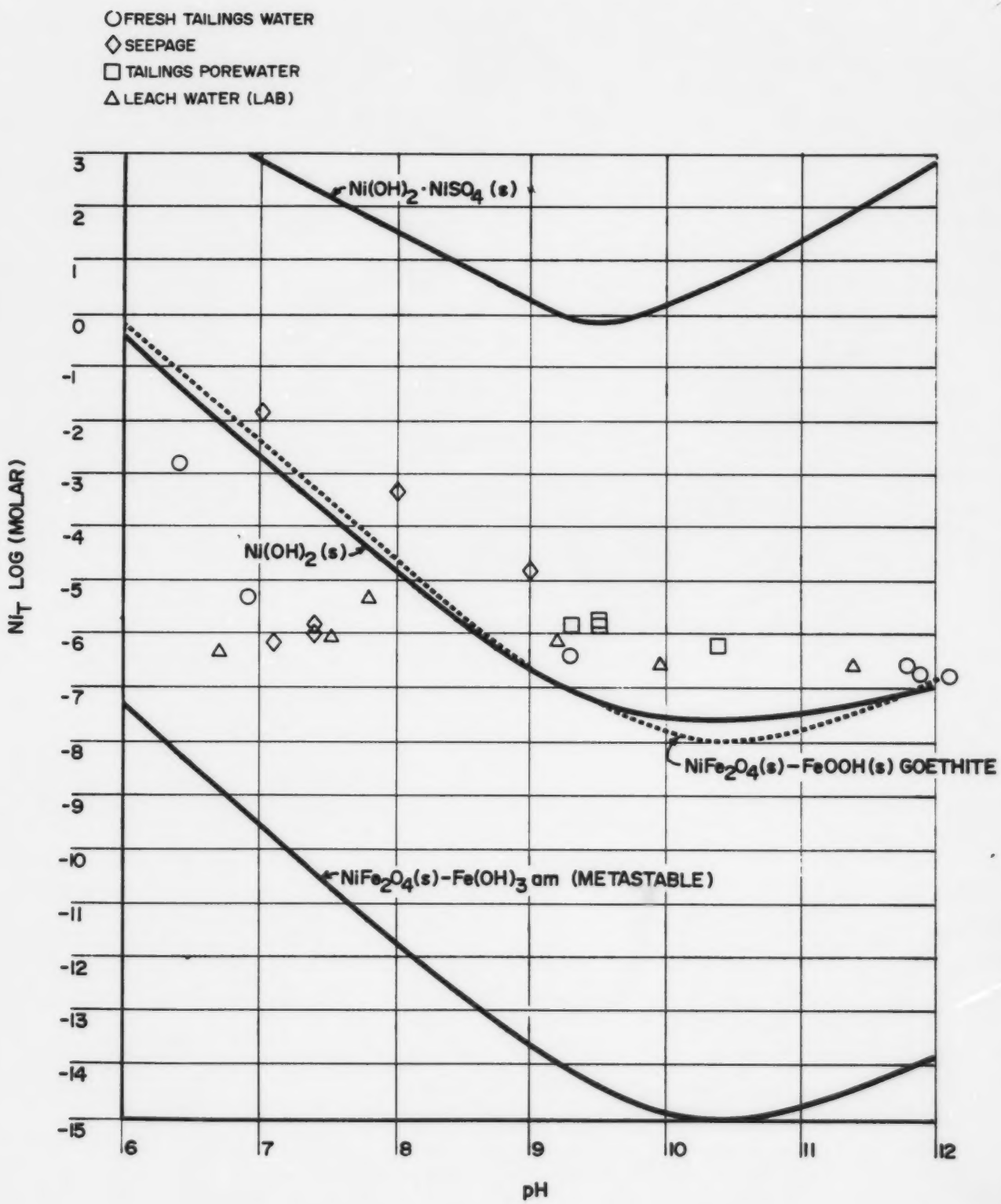
3.3 Cobalt, Molybdenum and Vanadium

The chemistry of each of these three elements is at least as complex as that of either nickel or arsenic. This section, therefore, is not an in-depth description of the equilibrium chemistry of these. The following provides a review of some of the general behaviour and important species involved. No attempt was made to model solubility controls.

3.3.1 Cobalt

Cobalt behaves in a manner similar to that of nickel. The ionic form of Co^{2+} in the +2 oxidation state is stable in natural waters. The important hydrolysis species are included in Table 3.6. Other important complexes in aqueous solution are similar to those for nickel. The hydroxide solid $Co(OH)_2$ has a similar solubility to that of nickel. In addition, however, the carbonate solid of cobalt (log K = -12.84) may be more important as a solubility control than that of nickel. And, of course, adsorption onto iron and manganese oxides provides an additional control on cobalt concentrations.

Figure 3.11: Total Nickel Concentrations as a Function of pH. Nickel Ferrite and $Ni(OH)_2$ Solid Solubility. Data are from Key Lake (Knight and Piesold, 1985)



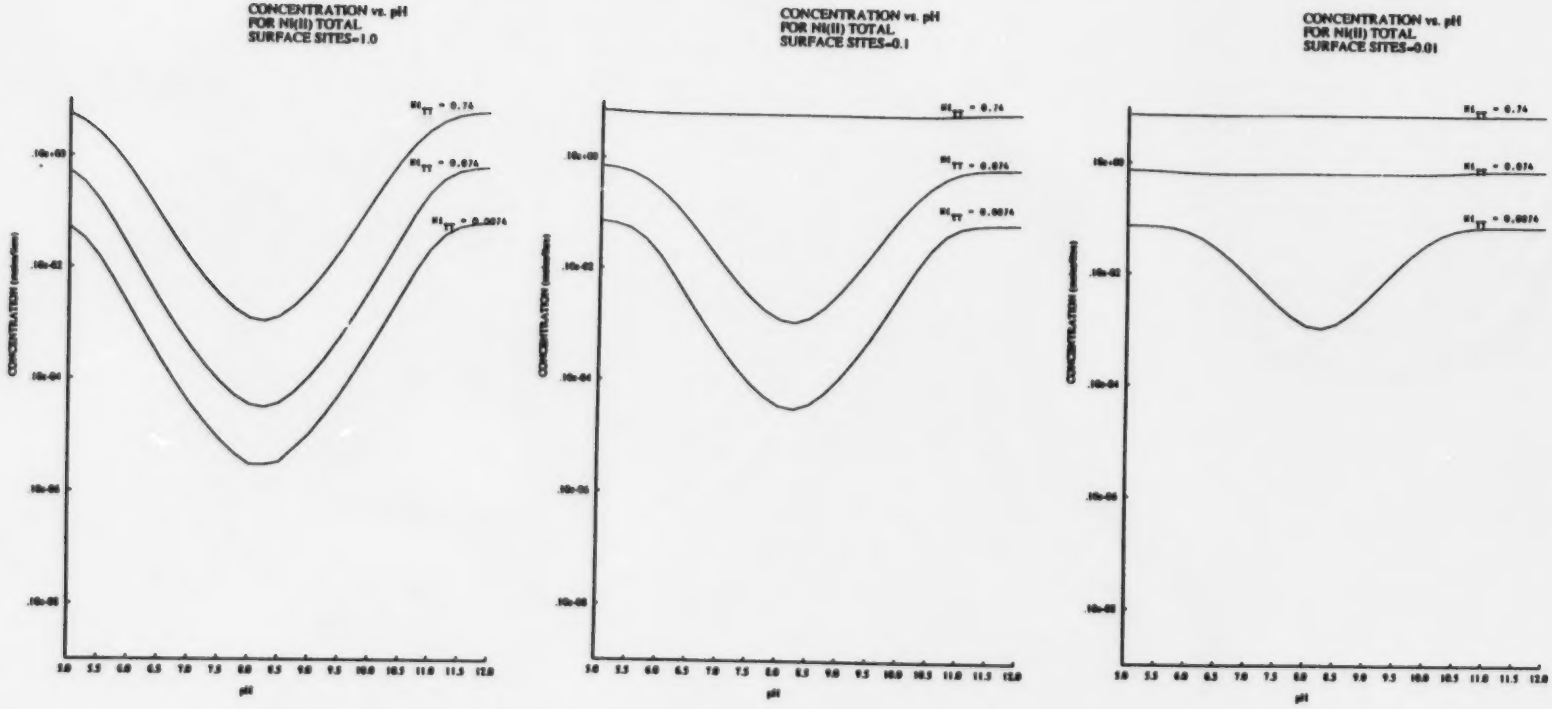


Figure 3.12: Adsorption of Nickel by Ferric Hydroxide

TABLE 3.6: COBALT REACTIONS AND CORRESPONDING STABILITY CONSTANTS

		log K
Hydrolysis*		
$Co^{2+} + H_2O$	$\rightleftharpoons CoOH^+ + H^+$	-9.65
$Co^{2+} + 2H_2O$	$\rightleftharpoons Co(OH)_2^o + 2H^+$	-18.8
$Co^{2+} + 3H_2O$	$\rightleftharpoons Co(OH)_3^- + 3H^+$	-31.5
$Co^{2+} + 4H_2O$	$\rightleftharpoons Co(OH)_4^{2-} + 4H^+$	-46.3
$2Co^{2+} + H_2O$	$\rightleftharpoons Co_2OH^{3+} + H^+$	-11.2
$4Co^{2+} + 4H_2O$	$\rightleftharpoons Co_4(OH)_4^{4+} + 4H^+$	-30.53
Solids		
$Co(OH)_2$ (pink-s) $+ 2H^+$	$\rightleftharpoons Co^{2+} + 2H_2O$	12.3
$Co(OH)_2$ (blue-s) $+ 2H^+$	$\rightleftharpoons Co^{2+} + 2H_2O$	13.8
$CoCO_3$	$\rightleftharpoons Co^{2+} + CO_3^{2-}$	-12.84

3.3.2 Molybdenum

The chemistry of molybdenum is complicated by various redox states and polynuclear speciation. A diagram showing the various stable species and solids as a function of Eh and pH is given in Figure 3.13. The polynuclear forms of Mo are important only below a pH value of about 5, and then only when total concentrations of Mo are greater than 10^{-4} M (Figure 3.14). The important protonation reactions are shown in Table 3.7. The most stable oxidation state is +6 which occurs in water as molybdate (MoO_4^{2-}). Molybdate solids can form with cations such as Pb, Cu, Bi and Ca for which thermodynamic data are available in the NBS tables (Wagman et al., 1982). In addition, coprecipitation of Mo with ferric and mangonous oxides has been recognized to be an efficient process that limits concentrations in solution.

3.3.3 Vanadium

Three possible oxidation states of vanadium may be stable in aqueous systems. The +5 state is stable in oxidizing conditions, the +4 form is intermediate and the +3 state is stable under reducing conditions. All oxidation states have stable hydrolysis complexes. The distribution of species in solution as a function of Eh and pH is given in Figure 3.15. The formation of polynuclear complexes also occurs for V (+5) at higher concentrations as shown in Figure 3.16. Some oxides of vanadium may be sparingly soluble, but no vanadium minerals are known to exist in pure form. The vanadate form (VO_4^{3-}) behaves in a similar manner to arsenate and phosphate and substitution is common, but a much smaller number of vanadate solids are known than either phosphates or arsenates. Adsorption by ferric hydroxides has been noted. A summary of vanadium reactions and equilibrium constants is given in Table 3.8.

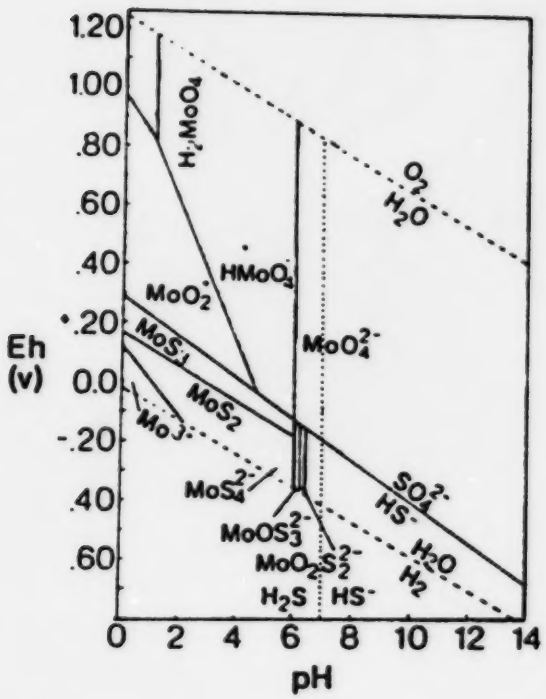


Figure 3.13: Eh-pH Diagram for Molybdenum with Total Mo = 10^{-6} M and total S^2 = 10^{-4} M (from Evans et al., 1974)

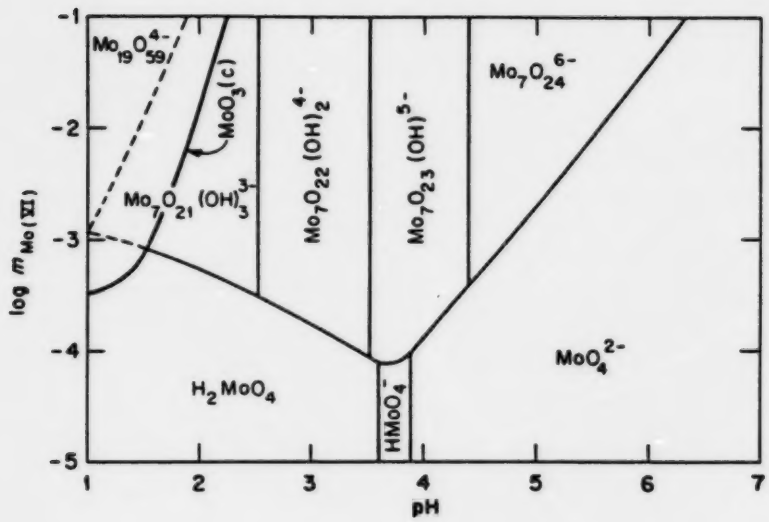


Figure 3.14: **Molybdate Species with pH (from Baes and Mismer, 1976)**

TABLE 3.7: MOLYBDENUM REACTIONS AND CORRESPONDING STABILITY CONSTANTS

		log K
Hydrolysis		
$MoO_4^{2-} + H^+$	$\rightleftharpoons HMoO_4^-$	3.7
$MoO_4^{2-} + 2H^+$	$\rightleftharpoons H_2MoO_4^o$	(7.5)
Solids		
MoO_3 (s) + H_2O	$\rightleftharpoons MoO_4^{2-} + 2H^+$	-12.06

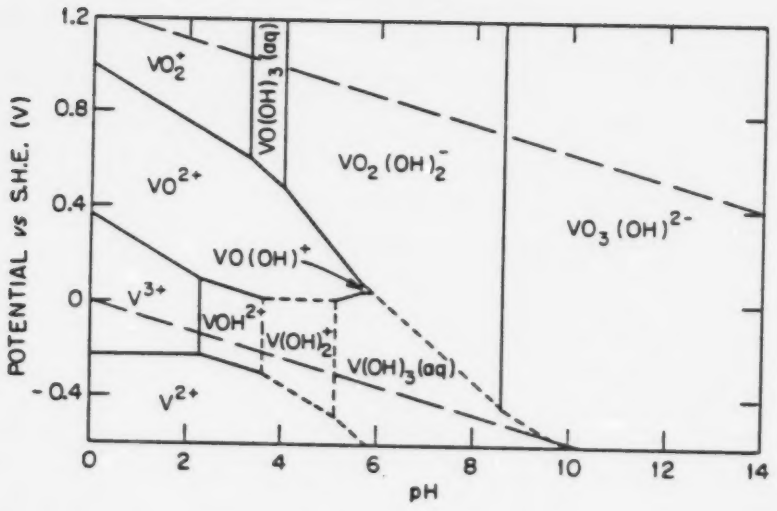


Figure 3.15: Eh-pH Diagram for Vanadium in Solution (from Baes and Mesmer, 1976)

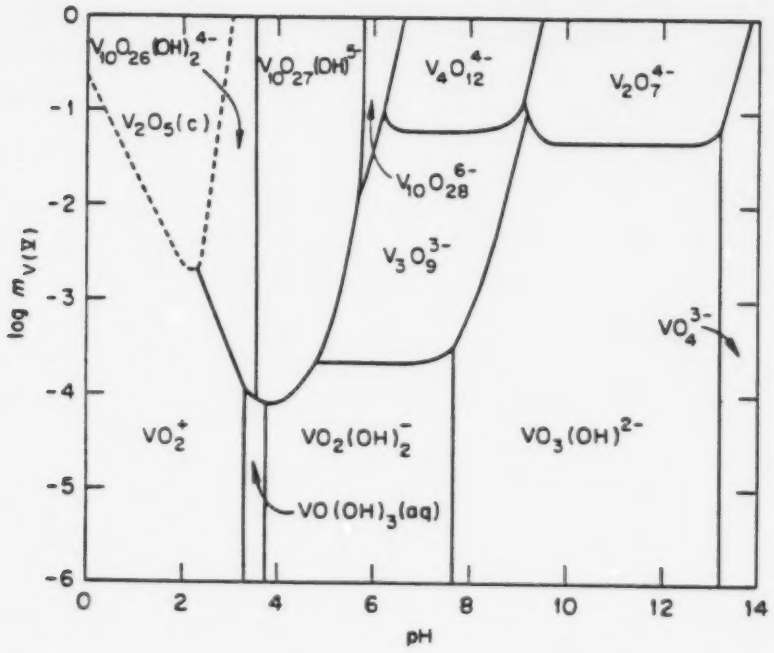


Figure 3.16: **Vanadate Species as a Function of pH (from Baes and Mesmer, 1976)**

TABLE 3.8: VANADIUM REACTIONS AND CORRESPONDING STABILITY CONSTANTS

		log K
Hydrolysis		
$VO_4^{3-} + H^+$	$\rightleftharpoons HVO_4^{2-}$	14.26
$VO_4^{3-} + 2H^+$	$\rightleftharpoons H_2VO_4^-$	22.81
$VO_4^{3-} + 3H^+$	$\rightleftharpoons H_3VO_4^o$	26.81
$VO_4^{3-} + 4H^+$	$\rightleftharpoons H_4VO_4^+$	34.11
$VO^{2+} + H_2O$	$\rightleftharpoons VO(OH)^+ + H^+$	-5.67
$2VO^{2+} + 2H_2O$	$\rightleftharpoons (VO)_2(OH)_2^{2+} + 2H^+$	-6.67
$V^{3+} + H_2O$	$\rightleftharpoons VOH^{2+} + H^+$	-2.26
$V^{3+} + 2H_2O$	$\rightleftharpoons V(OH)_2^+ + 2H^+$	(-6.0)
$V^{3+} + 3H_2O$	$\rightleftharpoons V(OH)_3^o + 3H^+$	(-11.2)
Solids		
$1/2V_2O_4$ (-s) $+ 2H^+$	$\rightleftharpoons VO^{2+} + H_2O$	4.28
$1/2V_2O_5$ (s) $+ H^+$	$\rightleftharpoons VO^{2+} + 1/2H_2O$	-0.66

4.0 HIGHLIGHTS AND DEFICIENCIES IN DATA

For reasons of the relative effort exerted in examining nickel and arsenic geochemistry compared to that for cobalt, molybdenum and vanadium, this discussion is limited to the first two constituents. In this in-depth review of thermochemical data and relevant environmental information on arsenic and nickel, it was apparent that some forms of data were known with precision while others were not. It is also evident that, although certain data are known precisely, they may not necessarily be of great importance when modelling the resulting concentrations in solution. It is important to distinguish the critical data as well as to define the major uncertainties inherent in the data, and to understand the implications of such uncertainty. The following discussion addresses these aspects of the thermochemical data for As and Ni.

4.1 High Confidence Data

Arsenic

The stability constants describing the protonation of dissolved arsenic species with pH are known with a high degree of certainty for both As(+5) and As(+3) species. These data are shown in Table 3.1. There are also some free-energy data for arsenic minerals, mainly the reduced forms, that is relatively precise. These include data on some sulphides and arsenides but for which equilibrium at earth-surface conditions is not meaningful. Other arsenic data are much less certain. Solubility data for many secondary solids may be in error by one order of magnitude or more.

Nickel

The hydrolysis of nickel in solution is fairly well defined. Stability constants describing the formation of $Ni(OH)^+$, $Ni(OH)_2^o$ and $Ni(OH)_3^-$ are precise (see Table 3.5). The data pertaining to the formation of $Ni(OH)_4^{2-}$ and polynuclear species are much less certain. These later species, however, are important at pH values greater than about 10 and when nickel concentrations are quite high. The solubility data for many soluble solids are relatively precise, but the equilibrium constant for the hydroxide $Ni(OH)_2$ is dependent on conditions of formations and therefore is not certain. Solubility may differ by up to three orders of magnitude, depending on conditions of formation of the solid and aging

history. Environmentally-formed $Ni(OH)_2$ may be less variable, but there are no data to substantiate this hypothesis.

The stability of complexes such as $NiSO_4^o$ and $NiCl^+$ are well known. The equilibrium constants for $NiHCO_3^+$ and $NiCO_3^o$ have not been measured and the estimates for these may be in error by orders of magnitude.

4.2 Critical Data and Major Uncertainties

It can be stated that, in general, the stability of solubility-limiting solids is much more critical in modelling solution concentrations than are data related to aqueous complexes. The errors involved in solubility data are much more significant than those for aqeuous complexes. For arsenic and nickel, it is evident that data for the solids are very imprecise, while that for the solution complexes are more certain.

Arsenic

No arsenic solids were found to be relevant in controlling solubility of As at pH values below about 11. The important data, therefore, involve the adsorption mechanism that is postulated to control arsenic concentrations in solution. These are not strictly thermodynamic data, but they are presented in this form for the adsorption reactions. The uncertainties involved in this approach are great, and it is unlikely that precise estimates of dissolved arsenic can be made with existing knowledge in heterogeneous systems such as uranium tailings.

Major uncertainties also exist because arsenate solids are known to occur in nature, but thermodynamic data for these are not available. It is quite possible, therefore, that solids control arsenic solubilities and yet have not been investigated. The case of ferric arsenate solids represents one example for which some evidence suggests solubility control, but has not been studied in detail. This is an area that warrants further investigation.

Nickel

Solid $Ni(OH)_2$ is known to form in nickel solutions. There is a major uncertainty, however, in the solubility product for the solid that forms under variable conditions. The

resulting nickel concentrations vary over three orders of magnitude as a result of the variation in stability data for this solid. This represents a critical uncertainty in predicting nickel solubility.

The other solid postulated to be involved in controlling nickel concentrations is the ferrite phase. Thermodynamic data for this solid are not very precise. In addition, the prediction of Ni concentrations from nickel ferrite solubility requires an estimate of ferric iron concentrations. Estimates of ferric iron control are extremely imprecise, adding to the overall uncertainty in predicting nickel behaviour. It is evident that further experimental work is required to better characterize the solids in the tailings environment.

Major uncertainty also exists in determining the effect of adsorption onto or coprecipitation of nickel with ferric hydroxides. This phenomenon appears to be important in controlling nickel concentrations in some environments.

5.0 CONCLUSIONS

Aqueous arsenic concentrations in the uranium tailings environment can be modelled by adsorption onto aluminum and ferric hydroxide solids. No definite solid controls are apparent below a pH of about 11. Preliminary evidence suggests that undifferentiated ferric arsenate solids may provide some control of arsenic concentrations in the neutral pH range. Thermodynamic data are not available, and some ambiguities exist.

Nickel concentrations in tailings pore water may be controlled by the solubility of nickel hydroxide solid in an unaged system. Later controls are not clear, but they could be associated with adsorption by ferric hydroxide material in the tailings. The resulting nickel concentrations are not easily modelled.

A review of the past and current literature has shown that no definitive controls exist for either arsenic or nickel in aqueous systems. Modelling is complicated by combinations of controls including solids and adsorption, and by sparse thermodynamic data. In addition, poorly characterized solids may play a role.

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APPENDIX A

Report by MCEL on the Ore and Milling Aspects of Uranium Tailings

GEOCHEMICAL BEHAVIOR OF VARIOUS NON-RADIONUCLIDE CONTAMINANTS IN URANIUM MILL TAILINGS

(Section by Melis Consulting Engineers Ltd.)

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GEOCHEMICAL BEHAVIOR OF VARIOUS NON-RADIONUCLIDES CONTAMINANTS IN URANIUM MILL TAILINGS

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GEOCHEMICAL BEHAVIOR OF VARIOUS NON-RADIONUCLIDE CONTAMINANTS IN URANIUM MILL TAILINGS

(Section by Melis Consulting Engineers Ltd.)

1.0 INTRODUCTION

This report by Melis Consulting Engineers Ltd. (MCEL) forms part of the National Uranium Tailings Program study on the geochemical behavior of various non-radionuclide contaminants in uranium mill tailings being carried out under contract to the Department of Supply and Services by Beak Consultants Limited of Mississauga, Ontario.

The pertinent items of the scope of work which are the responsibility of MCEL include a description of uranium ore characteristics for known Canadian nickel-arsenic type orebodies both for producing orebodies and future potential producers. Ore mineralogy is provided along with typical ore analysis and head grades where available.

The non-radionuclide contaminants identified in the study include nickel, arsenic, molybdenum, cobalt and vanadium. The dissolution characteristics of these elements in a typical uranium leaching circuit is detailed to provide an indication of the mobility of these elements during the uranium leaching process. The mineralogy of uranium tailings is presented to correlate the deportment of elements as precipitates in the waste treatment circuits of uranium mills.

2.0 URANIUM ORE CHARACTERISTICS

2.1 GENERAL

The nickel-arsenic type uranium orebodies in Canada are all located within the Athabasca Basin in northern Saskatchewan. These deposits are significantly higher grade than the uranium deposits in the Elliot Lake region of northern Ontario and are also accompanied by a significantly different mineralogical make-up.

Of the three northern Saskatchewan producers only Cluff Mining processes a relatively "clean" ore which does not contain arsenic or nickel minerals with the pitchblende uranium mineralization. The Key Lake deposit and the Collins Bay B-Zone deposit contain significant amounts of non-radionuclide contaminants with the uranium mineralization. The Rabbit Lake ore, which is nearly depleted at the Eldor Mines operation, is comparable to the Cluff Lake ore in light of its low nickel and arsenic content.

There is currently on-going uranium exploration in northern Saskatchewan with several nickel-arsenic bearing high-grade uranium deposits having been identified to date. By far the most important deposit in terms of total uranium content and grade is the Cigar Lake deposit. Other deposits of significance include the Midwest deposit, Dawn lake and McLean Lake.

2.2 MINERALOGY

Key Lake

The Key Lake mine, operated by Key Lake Mining Corporation of Saskatoon, Saskatchewan, is located approximately 240 km north of LaRonge, Saskatchewan, 70 km east-southeast of Cree Lake. The Key Lake uranium deposit consists of two separate orebodies, the Gaertner orebody and the Deilmann orebody. Both orebodies contain uranium mineralization associated with nickel arsenides.

The uranium ore minerals include euhedral and radially textured pitchblende [U_3O_8], and smaller amount of coffinite [$U(SiO_4)_{1-x}(OH)_{4x}$]. Gersdorffite [(Ni,Co)AsS] is the most abundant nickel mineral followed by niccolite [NiAs] and bravoite [$(Ni,Fe)S_2$]. Galena [PbS] of radiogenic origin is always present. Within the unaltered basement rocks pyrrhotite [$Fe_{1-x}S$] and chalcopyrite [$CuFeS_2$] have been observed. Extensive intergrowth of uranium and nickel minerals is present. Sooty pitchblende and coffinite can constitute the matrix for gersdorffite, millerite, niccolite and galena or vice versa.

Above the ore-bearing basement uranium-nickel mineralization occurs intermittently disseminated in porous and fractured sandstone and conglomerate. Chlorite schist is the main uranium-nickel bearing host rock with quartzite host having a distinctly lower grade. In both the chlorite and quartzite hosts limonite [$FeO(OH).nH_2O$], hematite [Fe_2O_3] and carbonates [CO_3] can accumulate in shear zones, cavities and fractures. Graphite [C] is present throughout the mineralization.

Collins Bay

The Collins Bay B-Zone uranium deposit, being mined by Eldor Mines, is situated on the west side of Wollaston Lake in northern Saskatchewan. The existing Rabbit Lake mill has been modified to enable processing of the Collins Bay ore which contains arsenic and nickel-bearing minerals.

The uranium mineralization in the B-Zone ore is made up of pitchblende [U_3O_8] and coffinite [$U(SiO_4)_{1-x}(OH)_{4x}$]. Associated mineralization includes gersdorffite [(Ni,Co)AsS], skutterudite [$(Co,Ni)As_2$], niccolite [NiAs], millerite [NiS], galena [PbS], chalcopyrite [$CuFeS_2$] and pyrite [FeS_2]. Elemental assemblages contain silver, arsenic, cobalt, chromium, copper, nickel, lead, titanium, vanadium and zirconium.

The Collins Bay A-Zone orebody contains pitchblende [U_3O_8] associated with rammelsbergite [$(Ni,Co,Fe)As_2$], pararammelsbergite [$NiAs_2$] and some galena [PbS] and sphalerite [ZnS].

The Eagle Point deposit, which forms part of the uranium ore reserves for the Eldor Mines operation, contains pitchblende [U_3O_8], coffinite [$U(SiO_4)_{1-x}(OH)_{4x}$], uranophane [$Ca(UO_2)_2(SiO_3)_2(OH)_2.5H_2O$] and boltwoodite [$K_2(UO_2)(SiO_3)_2(OH)_2.5H_2O$]. Associated minerals include gersdorffite [(Ni,Co)AsS], millerite [NiS], chalcocite [Cu_2S] and galena [PbS].

Cigar Lake

The Cigar Lake orebody is located approximately 115 km NE of the Key Lake Mine or 55 km WSW of Eldor Mines' operations at Rabbit Lake. The uranium in this high-grade deposit occurs as uraninite

[UO_2] and pitchblende (U_3O_8) with coffinite [$U(SiO_4)_{1-x}(OH)_{4x}$] being present in smaller quantities. The sulfo-arsenides of nickel and cobalt can locally be major components of the ore with the main minerals being gersdorffite [(NiCo)AsS], skutterudite [$(Co,Ni)As_2$], niccolite [NiAs], bravoite [$(Ni,Fe)S_2$], cobaltite [(Co,Fe)AsS], and rammelsbergite [$(Ni,CoFe)As_2$]. The sulfide minerals pyrite [FeS_2], marcasite [FeS_2], pyrrhotite [$Fe_{1-x}S$], smythite [$Ag\ AsS_2$], chalcopyrite [$CuFeS_2$], covellite [CuS], bornite [$Cu_5\ FeS_4$], galena [PbS], jordisite [MoS_2], and sphalerite [ZnS] are also present in varying but generally smaller amounts.

Midwest Deposit

The Midwest uranium deposit is located northwest of the Rabbit Lake minesite near the eastern edge of the Athabasca Basin. The principal minerals in this deposit include pitchblende [U_3O_8], coffinite [$U(SiO_4)_{1-x}(OH)_{4x}$], gersdorffite [(Ni,Co)AsS], niccolite [NiAs], rammelsbergite [$(Ni,Co,Fe)As_2$]. Also present are minor amounts of chalcopyrite [$CuFeS_2$], galena [PbS], bismuthinite [Bi_2S_3] polydimite [Ni_3S_4], and cobalt and silicate minerals. The pitchblende nickel-arsenide veins are associated with kaolinite-chlorite [$Al_4Si_4O_{10}(OH)_8$-$(Mg,Al,Fe)_{12}(Si,Al)_8O_{20}(OH)_{16}$] and sericite [$K_2Al_4Si_6Al_2O_{20}(OH,F)_4$].

Dawn Lake

The Dawn Lake deposit is also located northwest of the Rabbit Lake minesite. The Dawn Lake orebody is made up of several "pods" and hence the ore can be expected to vary in uranium grade and

elemental assemblage. The mineralogy of the ore basically consists of pitchblende [U_3O_8], uraninite [UO_2] and coffinite [$U(SiO_4)_{1-x}(OH)_{4x}$] as uranium minerals with nickel arsenides, carbonates and goethite [FeO(OH)] being present as other constituents. Host minerals include quartz [SiO_2], chlorite [$(Mg,Al,Fe)_{12}(Si,Al)_8O_{20}(OH)_{16}$], illite [$K_{1-1.5}Al_4Si_{7-6.5}Al_{1-1.5}O_{20}(OH)_4$], sericite [$K_2Al_4Si_6Al_2O_{20}(OH,F)_4$] and titatium oxides [$TiO_2$].

McLean Lake

The McLean Lake deposit is located in close proximity to the Dawn Lake deposit northwest of the Rabbit Lake minesite. The McLean ore is made up of four facies.

The sulphide facies consists of bravoite-pyrite [$(Ni,Fe)S_2$-FeS_2], coffinite [$U(SiO_4)_{1-x}(OH)_{4x}$],uraninite [UO_2], iron chlorite [$Fe_{12}(Si,Al)_8O_{20}(OH)_{16}$], illite [$K_{1-1.5}Al_4Si_{7-6.5}Al_{1-1.5}O_{20}(OH)_4$], siderite [$FeCO_3$] and chalcopyrite [$CuFeS_2$]. The arsenide facies occur as arsenide-illite intergrowths, pararammelsbergite [$NiAs_2$], niccolite [NiAs],gersdorffite [(Ni,Co)AsS] and safflorite [$(Co,Fe,Ni)As_2$]. A bleached facies contains nodular intergrowths of coffinite-pararammelsbergite and illite with subordinate nicollite, gersdorffite and arsenides. The oxide facies contains nodular intergrowths of coffinite-pararammelsbergite in hematized clay.

2.3 ORE ANALYSIS

Typical analysis of Key Lake, Collins Bay B-Zone, Cigar Lake and Midwest ores are given in Tables 2-1, 2-2, 2-3 and 2-4 respectively.

For comparison, analyses of elements of concern to this study are provided in Table 2-5 along with typical analysis of Elliot Lake ore and Cluff Lake ore. The significant content of non-radionuclide contaminants in the northern Saskatchewan nickel-arsenide uranium ores associated with the Athabasca Basin is evident from a comparison of the values listed in this table.

TABLE 2-1

TYPICAL ANALYSIS OF KEY LAKE ORE

Element	%	
	Gaertner Ore	Deilmann Ore
U_3O_8	2.0	2.9
Ra-226	222 Bq/g	N/A
SiO_2	50	50
Fe	3.5	3.0
S	1.0	0.8
Cu	0.03	0.09
Zn	0.08	0.03
Mo	0.006	0.03
V	0.08	0.09
Ni	2.5	1.1
Co	0.08	0.08
Ti	0.4	0.6
Al	9.0	10.3
As	1.5	1.1
Ca	0.4	0.4
Mg	3.0	2.9
Na	0.7	0.9
K	0.6	1.5
F	0.05	N/A
P_2O_5	0.16	0.15
CO_2	1.0	0.8
Cl	0.05	N/A

TABLE 2-2

TYPICAL ANALYSIS OF COLLINS BAY B-ZONE ORE

Element	%
U_3O_8	0.6
ThO_2	0.003-0.04
Fe	1-3
S	0.1
Mo	0.01-0.02
V	0.02-0.05
Ni	0.4
As	0.5
PO_4	0.02
CO_2	0.2
Ra-226(est)	60 Bq/g

TABLE 2-3

AVERAGE GRADE OF CIGAR LAKE ORE

Element	%
U_3O_8	14.5
Cu	0.7
Zn	0.04
Pb	1.2
Mo	0.14
Ni	1.0
Co	0.15
As	1.7
Ra-226(est)	1450 Bq/g

TABLE 2-4

AVERAGE GRADE OF MIDWEST ORE

Element	%
U_3O_8	2.2
Ra-226	275 Bq/g
L.O.I.	3.1
SiO_2	76
Fe	1.3
S	1.1
Cu	0.1
Zn	0.07
Mo	0.06
V	0.08
Ni	1.7
Co	0.2
Ti	0.3
Al	3.2
Mn	0.04
Cr	0.02
As	3.2
Ca	0.1
Mg	0.5
Na	0.1
K	1.2
F	0.05
P	0.03
CO_2	0.5
Cl	0.03
Zr	0.05
Rb	0.05
Sr	0.01

TABLE 2-5

ORE ANALYSIS COMPARISON

Ore	U_3O_8	Ni	As	Mo	Co	V
Key Lake (Gaertner)	2.0	2.5	1.5	0.006	0.08	0.08
Key Lake (Deilmann)	2.9	1.1	1.1	0.03	0.08	0.09
Collins Bay B-Zone	0.6	0.4	0.5	0.02	-	0.05
Cigar Lake	14.5	1.0	1.7	0.14	0.15	-
Midwest	2.2	1.7	3.2	0.06	0.2	0.08
Cluff Lake	0.7	0.003	0.001	0.02	-	0.02
Elliot Lake	0.1	0.003	<0.005	<0.001	0.005	<0.001

3.0 LEACHING CHARACTERISTICS

3.1 LEACHING PROCESS

The leaching process for nickel-arsenic uranium ores is not significantly different from other uranium acid leaching circuits although relatively high acid concentrations must be maintained to ensure high uranium extraction and to stabilize the leach liquor for preventing reprecipitation of uranium with other ions in solution. High oxidant addition is required in order to ensure sufficient oxidant for oxidizing all of the uranium to the hexavalent state in the presence of the non-radionuclide contaminants in the ore.

Acid leaching of the ground ore can be carried out in two stages, such as practiced at Key Lake, or in a single stage as planned for the Collins Bay ore and as proposed for the Midwest ore.

Key Lake

At Key Lake the ore is ground in a SAG mill to a mesh-of-grind of minus 500 micron. The ground ore is dewatered in a thickener to a pulp density of 50% solids with the addition of a flocculant to assist in settling. The thickened pulp is then pumped to a two-stage leaching circuit where the ore is leached with sulphuric acid under oxidizing conditions. Typical leaching conditions for the two stages are given in Table 3-1. A two-stage circuit is used in order to recycle acid solutions for reducing overall acid consumptions and to prevent formation of ferric arsenate in the pregnant solution by providing reducing conditions for the ferric ion contained in the recycled acid solution.

TABLE 3-1

KEY LAKE LEACH CIRCUIT CONDITIONS

	First Stage	Second Stage
Particle Size (% - 74 microns)	50	50
Pressure (k Pa)	atmospheric	600
Temperature (^{o}C)	25-30	60
Acid Concentration (g/L H_2SO_4)	>12	>40
Acid Consumption (kg/t H_2SO_4)	40	90
Pulp Density (% Solids)	15-20	50
Retention time (h)	1	4

The pulp first reports to the first-stage air-agitated pachucas where it is contacted with reclaimed acid solution (thickener overflow solution) from the second-stage leach and leached at atmospheric pressure and relatively low pulp density and temperature. Oxidant requirements in the first-stage leach are met by the injection of air used for agitation in the pachucas and the ferric content in the thickener overflow solution also acts as an oxidant for the leaching reactions. Acid requirements for the first-stage leach are met by the elevated acid level of the thickener overflow solution and by the addition of additional sulphuric acid as required.

The first-stage leach pulp is then pumped to the primary thickener where the thickener underflow is removed at 50% solids and pumped to the second-stage pressure leach feed tank. The overflow from the primary thickener is the pregnant solution which is pumped to solution pre-treatment ahead of the solvent extraction circuit.

Second-stage pressure leaching of the pre-leached ore slurry is carried out in a series of nine vertical pressure autoclaves. Sulphuric acid is added to the autoclave feed tank to provide the necessary acid levels for achieving high uranium extractions. Oxidant requirement is met by the injection of oxygen in the autoclaves. The second-stage leach slurry is then discharged into a surge tank for transfer to the eight stage counter-current-decantation (CCD) circuit.

The overflow from the first-stage thickener in the CCD circuit is the acid solution recycled to the first-stage leaching step. Additional sulphuric acid is added in the CCD circuit in order to maintain adequate acid levels for preventing loss of uranium by reprecipitation. Minewater is used as wash water to effectively wash uranium-containing solution from the leached ore. The underflow from the last CCD thickener is pumped to the tails neutralization circuit.

Collins Bay

The Collins Bay nickel-arsenic uranium ore will be leached in the existing Rabbit Lake leaching circuit. In this circuit ground ore will be leached with sulphuric acid at $50^{0}C$ under atmospheric pressure. Acidity levels in the leach will be maintained at 30 g/L $H_2 SO_4$. Sodium chlorate will be added at a rate of approximately 7.5 kg/t $NaClO_3$ in order to maintain oxidizing conditions in the leach.

The leach slurry will then be pumped to the existing Rabbit Lake CCD circuit for recovery of pregnant solution. The washed leach residue will be pumped to the tailings neutralization circuit and the pregnant solution will be clarified prior to reporting to the solvent extraction circuit.

Midwest

Two different acid leaching circuits have been proposed for the Midwest ore, a single stage pressure leach and a single stage atmospheric leach with the use of two oxidants. Proposed leaching conditions for both options are listed in Table 3-2.

In the pressure leach alternative ground ore at 30% minus 74 microns would be leached at $60^{0}C$ with an oxygen over-pressure of 450 kPa for a period of 4 hours. Terminal acidities would be maintained at 50 g/L H_2SO_4 with the addition of sulphuric acid to the autoclave feed resulting in an acid consumption of 100 kg/t.

TABLE 3-2

MIDWEST PROPOSED LEACH CIRCUIT CONDITIONS

Data	Pressure	Atmospheric
Particle size (% - 200 mesh)	30	30
Pulp density (% solids)	50	50
Temperature (^{o}C)	60	60
Pressure (kPa)	450	atmospheric
Time (h)	4	4
H_2SO_4 (kg/t)	100	80
Oxygen (kg/t)	20	-
Caro's acid (kg/t)	-	29
$NaClO_3$ (kg/t)	-	5
Terminal acidity (g/L)	50	50
Terminal emf (mV)	-400 to -430	-400

Pregnant solution would be recovered from the leach slurry in an eight stage CCD circuit. Washed leach residue would be neutralized with lime for disposal to the tailings area. Pregnant solution would be clarified prior to pumping to the solvent extraction circuit.

An atmospheric leaching circuit would leach the ore in air-agitated pachucas under atmospheric pressure maintaining acidity levels at 50 g/L H_2SO_4 with sulphuric acid. It has been proposed to supply oxidant requirements with Caro's Acid (H_2SO_5) formed on site by reacting hydrogen peroxide with sulphuric acid. In order to maintain proper acidity levels it would be necessary to use a small amount of sodium chlorate as oxidant since usage of Caro's Acid alone would result in elevated acidity levels. The leach slurry would be processed as in the pressure leach option to recover pregnant solution.

3.2 DISSOLUTION CHARACTERISTICS

The dissolution characteristics of nickel, arsenic, molybdenum, cobalt and vanadium in uranium acid leaching circuits are dependent on the behavior of their minerals in acid solution under oxidizing conditions. Typically for nickel-arsenic ores this infers a leach solution with acidity levels of 50 g/L H_2SO_4 and oxidation potentials of approximately -400 to 450 mV with solution temperature being 50-60^{o} C.

Nickel-Arsenic

The chemistry occurring in the leaching of nickel-arsenic uranium ores has been previously identified in metallurgical studies on Key Lake ore. Nickel and arsenic dissolution is claimed to occur according to the following general reactions:

$$NiAsS + 6.5\ O_2 + 3\ H_2O \longrightarrow 2\ NiSO_4 + 2\ H_3\ AsO_4$$
$$2\ NiAs + 2\ H_2SO_4 + 3.5\ O_2 + H_2O \longrightarrow 2\ NiSO_4 + 3\ H_3AsO_4$$
$$NiS + 2\ O_2 \longrightarrow NiSO_4$$

In the above reactions arsenides and sulphides are completely oxidized to arsenates and sulphates. Typical reactions for this oxidation are thought to be:

$$2\ NiAs + 2.5\ O_2 + 2\ H_2SO_4 \longrightarrow 2\ NiSO_4 + 2\ HAsO_2 + H_2O$$
$$HAsO_2 + .5\ O_2 + H_2O \longrightarrow H_3AsO_4$$
$$NiS + .5\ O_2 + H_2SO_4 \longrightarrow NiSO_4 + S^{o} + H_2O$$
$$S^{o} + 1.5\ O_2 + H_2O \longrightarrow H_2SO_4$$

The above reactions can account for leaching of nickel and arsenic from nickel arsenide minerals in a pressure leaching circuit under an oxygen atmosphere. Under atmospheric leaching conditions with sodium chlorate as oxidant the following reaction would be a typical reaction for nickel arsenide minerals:

$$6\ NiAs + 7\ NaClO_3 + 6\ H_2SO_4 + 3\ H_2O \longrightarrow 6\ NiSO_4 + 6\ H_3\ AsO_4 + 7\ NaCl$$

In the Key Lake leaching circuit ferric arsenate precipitation is encouraged by the use of a two-stage leach circuit as mentioned in Section 3-1. Under these leach conditions, or simply under leach conditions with high ferric iron in the leach solution, ferric arsenate precipitation occurs according to the following reaction:

$$Fe_2\ (SO_4)_3 + 2\ H_3\ AsO_4 \longrightarrow 2\ FeAsO_4 + 3\ H_2SO_4$$

This reprecipitation of ferric arsenate during leaching makes it difficult to estimate the amount of arsenic which remains in the leach residue in the form of the minerals originally present in the unleached ore.

Molybdenum-Cobalt-Vanadium

Molybdenum present in nickel-arsenide uranium ores mostly occurs as jordisite [MoS_2], an amorphous molybdenum sulphide, with minor occurrence of molybdenite [MoS_2]. Cobalt is associated with nickel in the nickel arsenide and nickel sulphide minerals and also partially occurs as cobaltite [(Co,Fe)As S]. Vanadium occurs as an amorphous, poorly crystallized, poorly defined compound.

Typical reactions which can account for the partial dissolution of molybdenum and cobalt in an acid leaching circuit under oxidizing conditions would therefore be:

$$MoS_2 + 4.5O_2 + 3\ H_2O \longrightarrow H_2MoO_4 + 2H_2SO_4$$
$$2\ CoAsS + 6.5O_2 + 3\ H_2O \longrightarrow 2\ CoSO_4 + 3\ H_3AsO_4$$

Typical reactions for vanadium dissolution are not postulated since its mineral make-up has not been identified. However after oxidation in an acid media the vanadium present in the ore will end up as the oxide V_2O_5.

3.3 DEPORTMENT OF ELEMENTS

The deportment of solubilized non-radionuclide elements in a uranium recovery circuit is not only influenced by the acid leaching step but also by the uranium (yellowcake) precipitation step and by the waste treatment circuits associated with uranium recovery. The deportment of nickel, arsenic, molybdenum, cobalt and vanadium in a uranium recovery circuit has therefore been estimated by calculating the distribution of these elements under assumed circuit conditions which would be typical of a uranium mill circuit for a nickel-arsenide uranium ore. The assumed circuit values and distribution calculations are summarized in Table 3-3. The deportment values for each element are depicted in Figure 3-1.

It should be noted that there would be some variation in these values depending on the nature of the ore being processed and on the specific process conditions being used for the ore. In particular the variability of arsenic dissolution would not only be dependent on the original mineral make-up of the ore but also on the extent of ferric arsenate precipitation in the leaching step.

It is also noted that the distributions given in this report have neglected the limited amount of non-radionuclide elements which would report with an ammonium sulphate product if ammonium sulphate crystallization is used for control of ammonia in mill effluents.

TABLE 3-3

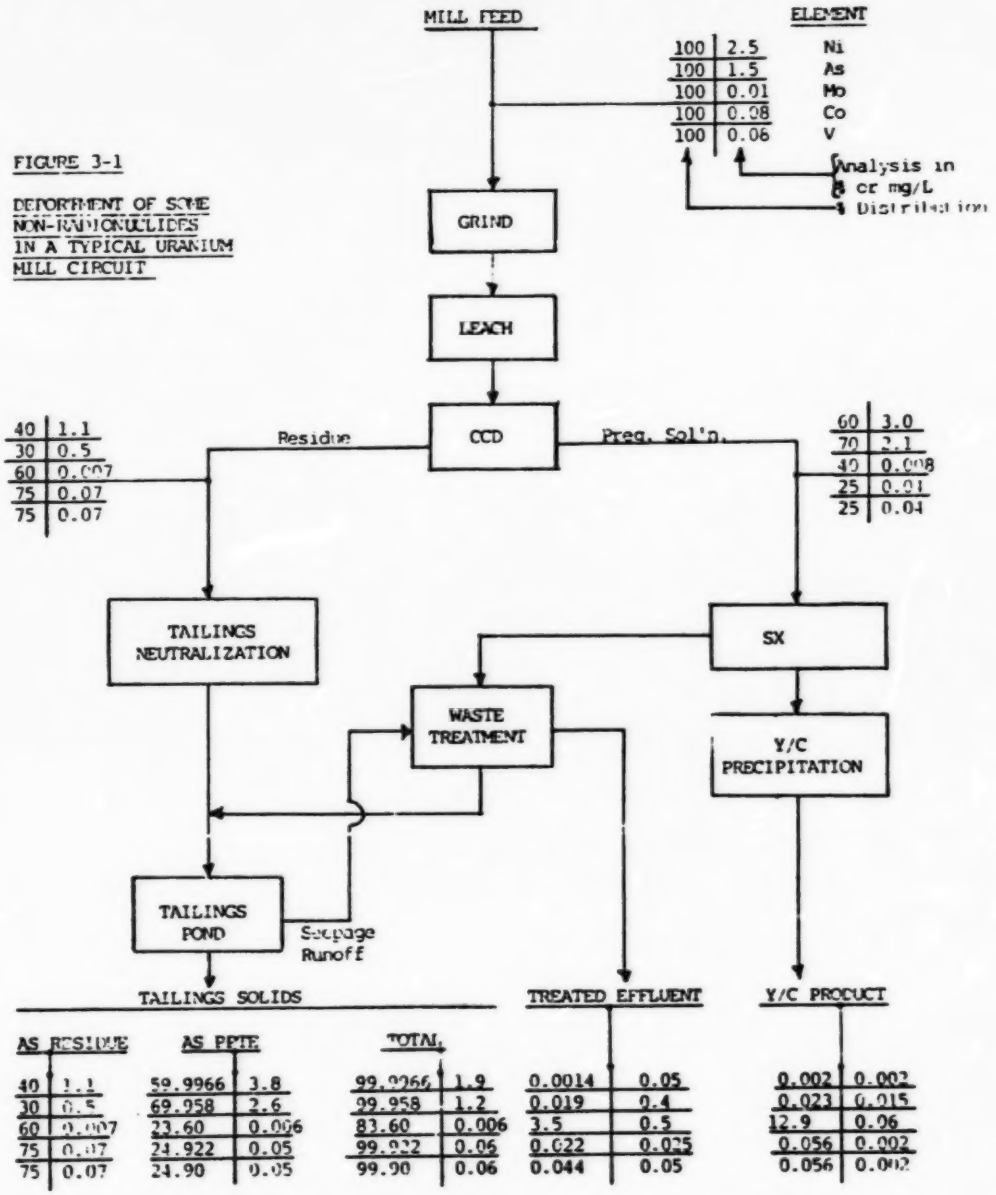
ASSUMED VALUES FOR DEPORTMENT CALCULATIONS*

Item	Ni	As	Mo	Co	V
Mill Head Grade (%)	2.5	1.5	0.01	0.08	0.08
% Dissolution	60	70	40	25	25
Pregnant Solution Analysis (g/L)	3.0	2.1	0.008	0.04	0.04
Yellowcake Analysis (%)	0.002	0.015	0.057	0.002	0.002
Treated Effluent Analysis (mg/L)	0.05	0.4	0.5	0.025	0.05
% Distr. to CCD Tails	40	30	60	75	75
% Distr. to Yellowcake	0.002	0.023	12.9	0.056	0.056
% Distr. to Treated Effluent	0.004	0.019	3.5	0.022	0.044
% Distr. to Total Tails	99.9966	99.958	83.6	99.922	99.90

* Other Assumptions:
- preg/ore wash ratio - 5/1
- annual yellowcake production - 6,307,300 kg
- treated effluent flow per year - 2,000,000 m^3
- weight loss in leach - 10%
- ratio of waste precipitate to mill feed - 0.4

FIGURE 3-1

DEPORTMENT OF SOME NON-RADIONUCLIDES IN A TYPICAL URANIUM MILL CIRCUIT



From the given estimated values it is apparent that the majority of the nickel, arsenic, cobalt and vanadium is reporting as tailings solids with only minor amounts being accounted for in the treated effluent or in the final yellowcake product. On the other hand an estimated 12.9% of the molybdenum originally present in the mill feed reports with the yellowcake and approximately 3.5% reports with the treated effluent if a molybdenum value of 0.5 mg/L is assumed for treated effluent quality.

Of the total nickel reporting with the tailings solids approximately 60% (as % of mill feed) is present in the form of precipitates. For arsenic it is estimated that at least 70% occurs in a precipitate form. This percentage would be higher if ferric arsenate precipitation is in fact occurring in the leaching step. For cobalt and vanadium the amount present as precipitate is 25%. Of the 83.6% molybdenum reporting to the tailings approximately 23.6% is in the form of precipitate.

The amount of each element (as % of mill feed) which remains present in the form of the original mineral composition in the tailings solids is 40% for nickel, 30% for arsenic (or less if ferric arsenate precipitation occurs in the leaching step), 60% for molybdenum, 75% for cobalt, and 75% for vanadium.

Typical reactions taking place during the neutralization and treatment of waste streams in a uranium recovery circuit, which would account for the distribution of elements in the form of precipitates, are as follows:

$2H_3AsO_4 + Fe_2(SO_4)_3 + 3Ca(OH)_2 \longrightarrow 2FeASO_4 + 3CaSO_4 \cdot 2H_2O$

$2H_3AsO_4 + 3Ca(OH)_2 \longrightarrow Ca_3(AsO_4)_2 + 6H_2O$

$NiSO_4 + Ca(OH)_2 + H_2O \longrightarrow Ni(OH)_2 + CaSO_4 \cdot 2H_2O$

$H_2MoO_4 + Ca(OH)_2 \longrightarrow CaMoO_4 + H_2O$

$CoSO_4 + Ca(OH)_2 + 2H_2O \longrightarrow CaSO_4.2H_2O + Co(OH)_2$

$3V_2O_5 + 10Ca(OH)_2 \longrightarrow 3Ca_2(VO_4)_2.Ca(OH)_2 + 9H_2O$

$V_2O_5 + 2Ca(OH)_2 \longrightarrow 2CaHVO_4 + H_2O$

$2CaHVO_4 \longrightarrow Ca_2V_2O_7 + H_2O$

In the presence of atmospheric oxygen the cobalt hydroxide precipitate [$Co(OH)_2$] would be at least partially oxidized to the aqueous oxide state [Co_3O_4 or Co_2O_3].

4.0 TAILINGS MINERALOGY

A mineralogical examination of Key Lake tailings in a separate NUTP study has summarized the mineral/chemical make-up of nickel-arsenide uranium tailings as follows:

quartz - SiO_2
gypsum - $CaSO_4.2H_2O$
bassanite - $2CaSO_4.H_2O$
graphite - C
ettringite - $Ca_6\ Al_2(SO_4)_3(OH)_{12}.26H_2O$
illite - $K_{1-1.5}Al_4\ Si_{7-6.5}Al_{1-1.5}O_{20}(OH)_4$
trichlorite - $(Mg,Fe)_{6-y-z}(Fe,Al)_3(Si_{4-x}Al_{4x})O_{10}(OH)_8$
calcium arsenate - $Ca_3\ (AsO_4)_2.3\ H_2O$
calcite - $CaCO_3$
gersdorffite - (Ni,Co)AsS
millerite - NiS
bravoite - $(Ni,Fe)S_2$
hematite - Fe_2O_3
iron-bearing sphalerite - ZnFeS
chalcopyrite - $CuFeS_2$
pyrite - FeS_2
galena - PbS
covelite - CuS
sphalerite - ZnS
linnarite - Co_3S_4
rutile - TiO_2
geothite - $HFeO_2$
nickel hydroxide - $Ni(OH)_2$
iron hydroxide - $Fe(OH)_3$
magnesium hydroxide - $Mg(OH)_2$
zinc hydroxide - $Zn(OH)_2$
lead hydroxide - $Pb(OH)_2$
copper hydroxide - $Cu(OH)_2$
cobalt hydroxide - $Co(OH)_2$

Other trace elements measured included P, V, Zr, Mn, Cd, Th, Mo, Y, Ba, Cr, La, Sr, Be.

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APPENDIX B

Compilation of a Consistent Thermodynamic Data Base for Arsenic and Nickel by Robert Lemire (AECL, Pinawa)

C-2347-0

CHEMICAL THERMODYNAMIC DATABASES FOR NICKEL AND ARSENIC

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CHEMICAL THERMODYNAMIC DATABASES FOR NICKEL AND ARSENIC

I. General Comments

Chemical thermodynamic databases have been constructed for nickel and arsenic. There are relatively few reliable data for nickel species beyond those noted in the U.S. National Bureau of Standards (NBS) compilation [1]. For arsenic, there have been several important papers [2-5] since 1964, the date of the last NBS review. These papers affect key values such as $S^\circ(As\text{-}\alpha)$ and the enthalpies of formation of the solid arsenic oxides. Because of the large number of elements that combine to form arsenic compounds of interest within the context of nickel-arsenic tailings, the databases for both nickel and arsenic were set up to be compatible with NBS auxilliary data (i.e., data for elements other than nickel and arsenic). The data for arsenic may or may not be compatible with NBS values for arsenic compounds not listed in Table 1.

Nickel

Values for $\Delta_f G^\circ(Ni^{2+})$ and $S^\circ(Ni^{2+})$ were taken from the NBS compilation [1]. These values are just within the experimental uncertainties of those later derived by Larson et al. [6]. The NBS values for $\Delta_f G^\circ(NiO)$, $\Delta_f G^\circ(NiCO_3(cr))$ and $S^\circ(NiO)$ were used. $S^\circ(NiCO_3(cr))$ was taken from Mah and Pankratz [7]. It should be noted that a nickel hydroxycarbonate mineral, zaratite, is known [8], but no suitable thermodynamic data are available for it.

As for many hydroxides, reported values for the solubility product of nickel hydroxide ($K_{sp} = \{Ni^{2+}\}/\{H^+\}^2$) vary by several orders of magnitude depending on the method of preparation and aging of the solid. The value $\Delta_f G^\circ(Ni(OH)_2,cr) = -447.2\ kJ \cdot mol^{-1}$ in the NBS tables [1] corresponds to a value of $\log_{10} K_{sp} = 12.73$. This is, apparently, based on an average of solubility product values in the literature. As discussed by Baes and Mesmer [9] and by Swaddle and Wong [10], it is probable that aged

$Ni(OH)_2$ (β-$Ni(OH)_2$) is stable at 25°C with respect to dehydration to NiO. The initial precipitate formed on addition of base to Ni^{2+} solution at 25°C, α-$Ni(OH)_2$, is more soluble than NiO. A value of $\Delta_f G°(\beta\text{-}Ni(OH)_2(s)) = -458.1\ kJ \cdot mol^{-1}$ has been selected on the basis of Gayer and Garrett's report [11] of $\log_{10} K_{sp} = 10.81$. For the more poorly defined α-$Ni(OH)_2$, a limiting value of $\log_{10} K_{sp} < 15$ has been selected ($\Delta_f G°(\alpha\text{-}Ni(OH)_2(s)) < -434\ kJ \cdot mol^{-1}$). Larger values of $\log_{10} K_{sp}$ have been reported [12], but in such cases it is not clear that hydrolysis equilibria were properly considered. The entropy of β-$Ni(OH)_2$ is that selected by Mah and Pankratz [7].

Values of $\Delta_f G°$ for the monomeric hydrolysis species of Ni^{2+} were calculated using Perrin's value [13] of $\log_{10} K_{11} = -9.86$, $\log_{10} K_{12} = -20.3 \pm 1.8$ from Tremaine and LeBlanc [14] and $\log_{10} K_{13} = -29.0$ from Gayer and Garrett [11]. The formation constant for the polymeric species, $Ni_4(OH)_4^{4+}$, was taken from Baes and Mesmer [9]. The entropy of $NiOH^+$ was calculated from the value given by Perrin [13] for the entropy of the hydrolysis reaction.

The entropy values for NiS and Ni_3S_2 in the NBS compilation [1] and in the monograph by Mah and Pankratz [7] are essentially the same. However, the enthalpy values differ markedly, with more recent data having been incorporated in the work of Mah and Pankratz. Therefore, we have used the enthalpy of formation values from this source with entropy values from the NBS tables to obtain $\Delta_f G°(\alpha\text{-}NiS) = -89.9\ kJ \cdot mol^{-1}$ and $\Delta_f G°(Ni_3S_2) = -212.2\ kJ \cdot mol^{-1}$.

No experimental data are available for the association constants of Ni^{2+} with HCO_3^- and CO_3^{2-}. Correlation methods can be used to estimate these constants [15]. The first association constants for the later first row transition element ions, M^{2+}, with oxalate are similar to the constants for association of the same cations with carbonate. Martell and Smith [16] (ex McAuley and Nancollas [17]) selected a value of $\log_{10} K_1 = 5.16$ for the Ni^{2+}/oxalate association at 25°C. Turner et al. [18] used that value to estimate $\log_{10} K_1 = 5.37$ for the Ni^{2+}/carbonate association equilibrium. This gives $\Delta_f G°(NiCO_3(aq)) = -604 \pm 6\ kJ \cdot mol^{-1}$, where the uncertainty is our

estimate, and reflects the lack of agreement between the various empirical methods for calculating this constant.

The stable hydrated nickel sulphate in contact with liquid water at 25°C is $NiSO_4 \cdot 7H_2O$, and values for this solid are from reference 1. The NBS value [1] for $\Delta_f G^\circ(NiSO_4(aq))$, -803.3 $kJ \cdot mol^{-1}$, reflects an association constant, $\log_{10} K = 2.28$, similar to the $\log_{10} K = 2.32$ selected by Smith and Martell [16], and we use the NBS value. For $NiCl^+$ we use $\log_{10} K = 0.72$ for the association constant (from Turner et al. [18]). This results in $\Delta_f G^\circ(NiCl^+) = -181.1$ $kJ \cdot mol^{-1}$.

Sadiq and Enfield indicate [19] that $NiFe_2O_4$ may be important in controlling the nickel concentration in groundwaters. Assessed values for $\Delta_f G^\circ(NiFe_2O_4)$ vary in the literature and include -959 $kJ \cdot mol^{-1}$ [7], -969 $kJ \cdot mol^{-1}$ [20], and -973 $kJ \cdot mol^{-1}$ [1]. Furthermore, the marked disagreement in the literature as to $\Delta_f G^\circ(Fe^{3+})$ [21] means calculated nickel concentrations based on $NiFe_2O_4$ solubility can also depend critically on this value. The NBS value for $\Delta_f G^\circ(NiFe_2O_4(s))$ is included in Table 1, but should only be used in conjunction with NBS values for other iron(III) solids, and even then should be used with extreme caution.

Arsenic

The value for $S^\circ(\alpha\text{-As})$ in the NBS compilation [1] is 35.1 $J \cdot K^{-1} \cdot mol^{-1}$. We have chosen $S^\circ(\alpha\text{-As}) = 35.7$ $J \cdot K^{-1} \cdot mol^{-1}$ based on more recent heat capacity data, as selected by Hultgren et al. [2].

The work of Beezer and coworkers [3,4] provides values of $\Delta_f H^\circ(As_2O_3, oct., cryst.)$ and $\Delta_f H^\circ(As_2O_5, cryst.)$ based on similar experimental methods. Thus, the relative enthalpies of formation for these solids should be consistent. The values were recalculated from the raw data of reference 3 using auxilliary data from reference 1. $\Delta_f H^\circ(As_2O_3, oct., cryst.) = -666.4 \pm 0.9$ $kJ \cdot mol^{-1}$ and $S^\circ(As_2O_3, oct., cryst.) = 107.41$ $J \cdot K^{-1} \cdot mol^{-1}$ from Chang and Besteel [5] were combined with our selected $S^\circ(\alpha\text{-As})$ and $S^\circ(O_2)$ [1] to give $\Delta_f G^\circ(As_2O_3, oct., cryst.) = -585.4$ $kJ \cdot mol^{-1}$. The monoclinic form of As_2O_3 has a more positive enthalpy of

formation (by 1.84 $kJ \cdot mol^{-1}$ [5]) and $S^\circ(As_2O_3, mono.) = 113.33\ J \cdot K^{-1} \cdot mol^{-1}$; hence, $\Delta_f G^\circ(As_2O_3, mono.) = -585.3\ kJ \cdot mol^{-1}$. $S^\circ(As_2O_5) = 105.4\ J \cdot k^{-1} \cdot mol^{-1}$ from Anderson [22], and with $\Delta_f H^\circ(As_2O_5) = -925.1 \pm 1.5\ kJ \cdot mol^{-1}$ [3], a value of $\Delta_f G^\circ(As_2O_5) = -782.3\ kJ \cdot mol^{-1}$ is calculated.

Schuhmann [23] obtained a solubility of 0.2067 $mol \cdot kg^{-1}$ of arsenic over solid As_2O_3 and, hence, $\Delta_r G = 7.82\ kJ \cdot mol^{-1}$ for

$$As_2O_3 + H_2O = 2HAsO_2 \quad .$$

Using $\Delta_f G^\circ(As_2O_3) = -585.4\ kJ \cdot mol^{-1}$, a value of $\Delta_f G^\circ(HAsO_2) = -407.4\ kJ \cdot mol^{-1}$ (or $\Delta_f G^\circ(H_3AsO_3) = -644.5\ kJ \cdot mol^{-1}$) is calculated. The entropy of H_3AsO_3 was calculated from the reported [3] $\Delta_r H = 26.6\ kJ \cdot mol^{-1}$ for

$$As_2O_3(oct., cryst.) + 3H_2O = 2H_3AsO_3 \quad .$$

The equilibrium constant for the reaction

$$I_3^- + H_3AsO_3 + H_2O = H_3AsO_4 + 2H^+ + 3I^-$$

was reported in Latimer [24] as 0.16. Thus, $\Delta_r G = 4.54\ kJ \cdot mol^{-1}$ and $\Delta_f G^\circ(H_3AsO_4) = -773.8\ kJ \cdot mol^{-1}$. The entropy of H_3AsO_4 was calculated using $\Delta_r H = -360.5\ kJ \cdot mol^{-1}$ [3] for

$$2H_3AsO_3 + O_2 = 2H_3AsO_4 \quad .$$

The Gibbs energies for the deprotonated forms of H_3AsO_3 were calculated using $pK_1 = 9.23$ [25], $pK_2 = 12.13$ [26] and $pK_3 = 13.4$ [26]. The deprotonation constants for H_3AsO_4 were taken equal to those selected by Smith and Martell [16]. The enthalpies of deprotonation of H_3AsO_3, H_3AsO_4, $H_2AsO_4^-$ and $HAsO_4^{2-}$ from reference 25 were used to calculate $S^\circ(H_2AsO_3^-)$, $S^\circ(H_2AsO_4^-)$, $S^\circ(HAsO_4^{2-})$ and $S^\circ(AsO_3^{3-})$, respectively. Latimer [24], from a recalculation of the data of Washburn and Strachan [27] by Randall [28], reported pK = 14.3 for

$$H_3AsO_3 = AsO^+ + OH^- + H_2O \quad .$$

This was used to calculate $\Delta_f G^\circ(AsO^+) = -168.5$ kJ·mol^{-1}.

Johnson et al. [29] recently reported chemical thermodynamic data for β-As_4S_4, α-As_4S_4 and As_2S_3, and reviewed difficulties found with other literature data for these compounds. The values for these solids have been taken directly from reference 29. Robins [30] has noted Gibbs energies for AsS_2^-, $H_2As_2S_4(aq)$ and $HAs_2S_4^-$ from an unpublished study of the solubility of As_2S_3. These values have been included in the database, but it is not certain what auxilliary thermodynamic data were used in deriving these numbers.

Gibbs energy values for several calcium arsenates and arsenites have been reported by Nishimura et al. [31]. We have used the solubility results of these workers to calculate Gibbs energy values for $CaH_4(AsO_4)_2$, $CaHAsO_4$, $Ca_5H_2(AsO_4)_4$, $Ca_3(AsO_4)_2$, $Ca_3(AsO_4)_2 \cdot Ca(OH)_2$, $Ca(AsO_2)_2$ and $Ca(AsO_2)_2 \cdot Ca(OH)_2$ that are consistent with our database. The value of $\Delta_f G^\circ(Ca_3(AsO_4)_2 \cdot Ca(OH)_2)$ given by Robins [30] and attributed to reference 31 was assumed to be incorrect. It is not clear in this work, or in other papers by Robins [30,32] what experimental uncertainties should be assigned to the solubilities, and to the pH values at which different solids become stable.

Chukhlantsev [33] reported solubility products for several metal arsenates including $Ni_3(AsO_4)_2$, $Mn_3(AsO_4)_2$ and $AlAsO_4$ from experiments done at 20-22°C. The original solubility products were calculated using slightly different equilibrium constants for arsenic acid deprotonation than are used here. Nevertheless, this causes a difference of < 2 kJ·mol^{-1}, well within the experimental uncertainties. Thus, the reported solubility products were used with our value of $\Delta_f G^\circ(AsO_4^{3-})$ and NBS [1] value of $\Delta_f G^\circ$ for the metal ions to derive Gibbs energies of formation for these solid arsenates.

Robins reported solubility equations for $BaHAsO_4$ and $Ba_3(AsO_4)_2$ [32]. Using these with our Gibbs energies for the arsenic oxy-anions and the NBS value for $\Delta_f G^\circ(Ba^{2+})$, $\Delta_f G^\circ(BaHAsO_4) = -1314$ kJ·mol^{-1} and $\Delta_f G^\circ(Ba_3(AsO_4)_2) = -3096$ kJ·mol^{-1} are calculated. The latter value is

markedly different from that given in reference 32, but is similar to the value reported in a later paper [30] by the same author.

Values for the Gibbs energies of formation of several magnesium and iron arsenates were appended to our database using values noted by Robins [30] with a correction applied for the differences in $\Delta_f G°(AsO_4^{3-})$ and $\Delta_f G°(HAsO_4^{2-})$ between the two databases. The same reservations exist with respect to the values for the iron solids as were noted above for $NiFe_2O_4$.

Table 1

Database[1]

Substance	$\Delta_f G°$/kJ·mol^{-1}	S°/J·K^{-1}·mol^{-1}
$O_2(g)$	0	205.138
$H_2(g)$	0	130.684
OH^-	-157.244	-10.75
$H_2O(l)$	-237.129	69.91
Cl^-	-131.228	56.5
HS^-	12.08	62.8
$H_2S(aq)$	-27.83	121.
SO_4^{2-}	-744.53	20.1
$CO_2(g)$	-394.359	213.74
CO_3^{2-}	-527.81	-56.9
Mg^{2+}	-454.8	-138.1
Ca^{2+}	-553.58	-53.1
Ba^{2+}	-560.77	9.6
Al^{3+}	-485.	-321.7
Mn^{2+}	-228.1	-73.6
Ni	0	29.87
Ni^{2+}	-45.6	-128.9
NiO	-211.7	37.99
α-$Ni(OH)_2$	< -434	
β-$Ni(OH)_2$	-458.1	80.0
$NiOH^+$	-226.4	-46.
$Ni(OH)_2(aq)$	-404	
$Ni(OH)_3^-$	-591	
$Ni_4(OH)_4^{4+}$	-972.6	
$NiCO_3(cr)$	-612.5	84
$NiCO_3(aq)$	-604	
NiS	-89.9	52.97
Ni_3S_2	-212.2	133.9

.../continued

Table 1 (continued)

Database[1]

Substance	$\Delta_f G°$/kJ·mol^{-1}	$S°$/J·K^{-1}·mol^{-1}
$NiSO_4 \cdot 7H_2O$	-2461.83	378.94
$NiSO_4$(aq)	-903.3	-18.0
$NiCl^+$	-181.1	
$NiFe_2O_4$	-973.1[2]	131.8
As	0	35.7
As_2O_3(oct.,cryst.)	-585.4	107.41
As_2O_3(mono.,cryst.)	-585.3	113.33
As_2O_5	-782.3	105.4
AsO^+	-168.5	
$HAsO_2$	-407.4	120.4
H_3AsO_3	-644.5	190.3
AsO_2^-	-354.7	36.3
$H_2AsO_3^-$	-591.8	106.2
$HAsO_3^{2-}$	-522.6	
AsO_3^{3-}	-446.1	
H_3AsO_4	-773.8	190.3
$H_2AsO_4^-$	-761.0	122.5
$HAsO_4^{2-}$	-721.3	0.1
AsO_4^{3-}	-655.6	-159.2
As_2S_3	-91.	164.
α-As_4S_4	-132.	248.
β-As_4S_4	-130.	254.
AsS_2^-	-23.2[3]	
$H_2As_2S_4$	-131.4[3]	
$HAs_2S_4^-$	-101.3[3]	
$CaH_4(AsO_4)_2$	-2069.	
$CaHAsO_4$	-1295.	

.../continued

Table 1 (concluded)

Database[1]

Substance	$\Delta_f G°$/kJ·mol^{-1}	$S°$/J·K^{-1}·mol^{-1}
$Ca_5H_2(AsO_4)_4$	-5665.	
$Ca_3(AsO_4)_2$	-3076.	
$Ca_3(AsO_4)_2 \cdot Ca(OH)_2$	-3990.	
$Ca(AsO_2)_2$	-1302.	
$Ca(AsO_2)_2 \cdot Ca(OH)_2$	-2235.	
$Ni_3(AsO_4)_2$	-1594.	
$Mn_3(AsO_4)_2$	-2160.	
$AlAsO_4$	-1231.	
$Ba_3(AsO_4)_2$	-3096.	
$BaHAsO_4$	-1314.	
$Mg_3(AsO_4)_2$	-2789.	
$MgHAsO_4$	-1194.	
$FeAsO_4$	-776.[2,3]	
$FeHAsO_4$	-862.[2,3]	
$Fe_3(AsO_4)_2$	-1781.[2,3]	

(1) Extra (insignificant) figures are reported for many of the arsenic species to minimize rounding errors in future calculations.

(2) Difficulties with the iron database mean these values should be used with extreme caution.

(3) May not be NBS consistent as it depends on the choice of auxilliary data used by the authors of reference 30.

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